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# Environmental Lead and Nickel Contamination of Tank Rainwater in Esperance, Western Australia: An Evaluation of the Cleaning Program

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#### Abstract

A significant number of birds in the port town of Esperance, Western Australia died in the summer of 2006/2007 and elevated lead levels were found in the kidneys, livers and brains of autopsied birds. These elevated lead levels alerted Government authorities to investigate the public health impacts of potential lead contamination in the community resulting from transport of lead carbonate from the Esperance Port. Water samples from domestic rainwater collection systems were collected to determine the extent of heavy metal contamination; 19% and 24% of tanks had lead and nickel levels above the Australian Drinking Water Guidelines. The aim of this study was to evaluate whether cleaning of rainwater tanks had reduced exposure to lead and nickel contamination in the community. Follow-up sampling of 176 tanks across Esperance indicated that that there had been reductions in both lead and nickel concentrations, but that the reduction has been greater for nickel concentrations. The reduction in nickel concentration was significantly associated with cleaning status, whereas this was not the case for lead. Proximity to the Esperance Port was an important determinant of lead concentration. Tank and roof characteristics did not significantly influence the follow-up lead concentrations. The results suggested that there was ongoing contamination of rainwater tanks from the environment.

Keywords: Lead Carbonate, Lead, Nickel, Rainwater Tanks, Environmental Exposure, Australia, Shipping Port

## 1. Introduction

In early 2007 residents and health authorities in Western Australian became concerned about the potential health impact of environmental lead exposure in the port town of Esperance, located on the Southeast coastline of Western Australia (WA). The population of the Shire of Esperance is approximately 13,000 and while the Shire covers an area of 42,450 square kms [1], the majority of the population lives in the Esperance town site. In April 2005 the Esperance Port Authority (EspPA) began shipping lead carbonate through the Esperance Port [2]. The lead was transported via rail from a mine site near Wiluna almost 900kms to the north. In December 2006 a significant number of bird deaths was reported and by the end of January 2007 up to 4000 birds were estimated to have had died [3]. High levels of lead were found in the livers, kidney and bones of dead birds. While lead was later determined unlikely to be the cause of the bird deaths, the elevated lead levels in these birds alerted Government authorities to investigate the potential public health impacts of lead contamination in the community. The EspPA put an immediate stop to any further shipments of lead carbonate from the Port [2].

The health effects of environmental lead exposure are well recognised with more recently attention focussed upon the health effects of lead exposure of  $10\mu g/dL$  or less in blood [4]. In 2005, the United States Centers of Disease Control and Prevention concluded that the weight of evidence supports an inverse association between blood lead levels of less than  $10\mu g/dL$  and cognitive function in children, but that it is as yet unclear re-



garding the size of effect [5]. Currently the Australian standards for blood lead are under review, but the intervention level for community-wide prevention strategies set by both the World Health Organisation and the United States Centre of Disease Control and Prevention is  $10\mu g/dL$ . The Western Australian Department of Health established a precautionary intervention level of  $5\mu g/dL$ , in acknowledgment of the community concerns about chronic exposure to lower lead levels, particularly among children [2].

Between March and August 2007 blood testing was offered to all residents and 2,219 blood samples were taken. Thirty-three samples had lead levels of  $10\mu g/dL$  or more. Seven of the 404 children aged less than five years had blood lead levels of  $10\mu g/dL$  or more [6].

While lead exposure through air and dust were considered important exposure pathways, there was just one air monitoring station in Esperance. Hence it was not possible to characterise the extent and distribution of lead contamination across the town site using these data. Tank rainwater provided an alternative sampling framework for this purpose. A large proportion of households across the Esperance township collect rainwater from domestic roof catchments to supplement their mains water supply. The domestic roofs served as a catchment for airborne and dust-borne lead contamination that was the washed into the tanks. Thus water from rainwater tanks was potentially an important source of lead exposure.

As part of the investigation into the extent of lead contamination, the Department of Health, in conjunction with the Shire of Esperance, tested 1,539 rainwater tanks for heavy metals (Figure 1). The results of this tank rainwater testing showed that lead levels in rainwater exceeded the Australian Drinking Water Guidelines (ADWG) for lead (0.01mg/L) in 285 (19%) of tanks. Nickel levels in 369 (24%) of rainwater tanks also exceeded the ADWG (0.02mg/L) [7,8].

Subsequently, the EspPA coordinated the cleaning of rainwater tanks and gutter systems for 1) residences identified with high lead levels in their tank rainwater sample and 2) tanks in the area identified by the Department of Health as more likely to have been impacted by lead pollution. The cleaning process involved: draining water from the tanks and pressure cleaning of the internal sides and bottom of the tank; vacuuming sludge residues



Figure 1. Location of rainwater tanks that were eligible for re-sampling, Esperance, October 2007.

out of the tank; and pressure cleaning gutters and the bottom part of roof area.

A total 423 tanks were cleaned as a part of this follow up program.

This paper reports on the follow up sampling undertaken to evaluate the rainwater tank cleaning program. The aims were to determine whether cleaning of rainwater tanks had been successful in reducing the lead and nickel levels to below the ADWG for lead (0.01mg/L) and nickel (0.02mg/L) and, if the levels remained high, what factors contributed to those elevated levels.

#### 2. Methods

#### 2.1. Study Population

A subset of rainwater tanks in Esperance were selected from initial population of rainwater tanks that weretested as part of the ongoing investigation of lead contamination in Esperance (Figure 1). Tanks in the suburb of Castletown (outside the grid area of Figure 1) were excluded in this follow-up investigation because this area was at low risk of lead contamination. The final study area contained 806 rainwater tanks that were eligible for retesting.

The study area was stratified by a 1 km square grid, resulting in 25 cells (Figure 1). A random sample of 236 tanks was selected from across the grids, proportional to the number of rainwater tanks initially tested in each grid. Consent to sample tanks as well as access to the property was gained for 179 tanks out of the 236 tanks.

#### 2.2. Water Sampling and Analysis

Baseline water samples were collected by the Department of Health and the Shire of Esperance between April and June 2007. Follow-up samples were collected after the period during which rainwater tanks had been cleaned. The follow-up samples were collected by the Department of Health and the Shire of Esperance from 15 to 29 October 2007 and taken from tanks that were cleaned and those that were not.

All samples were analysed for lead and nickel concentrations by the NATA accredited Chemistry Centre (Western Australia) using the method, 3120B Inductively Coupled Plasma Method from the Standard Method for the Examination of Water and Wastewater [9].

#### 2.3. Rainwater Tank Data

When the baseline samples were collected, data regarding the tank and catchment characteristics were obtained by the officer taking the sample. For 143 households, the resident was also surveyed to obtain additional information on: location; roof catchment material-tile, asbestos cement, Colourbond, zincalume; condition of roof catchment; gutters material, tank material-zincalume, galvanised iron, plastic, concrete, other; condition of the rainwater tank; presence of first flush diverter; opening on tank roof; other possible sources of lead including lead flashing, gutter type, etc.; date on which the tank was last cleaned, if not cleaned by EspPA.

Ninety-seven tanks were cleaned by EspPA between May and August, 2007. In the survey of residents (n= 143), an additional 29 tanks were reported to have been cleaned privately between March and September of 2007. The time between cleaning and the second sample ranged from 6 to 33 weeks, with a mean of 19 weeks.

#### 2.4. Statistical Analysis

Descriptive statistics for lead and nickel concentrations and changes over time were determined. Medians are presented because the lead and nickel concentrations were skewed towards zero. These results were compared with the ADWG, that is 0.01mg/L for lead and 0.02mg/L for nickel.

Results were mapped using the ESRI ArcMap software. Smooth grids of the testing results were achieved with ESRI Spatial Analyst, using the kernel density tool that transforms point data into a smoothed grid via a moving window technique [10].

Tank and roof characteristics, cleaning status and distance from the Port were compared across lead and nickel samples above and below the ADWG. The relationships between the lead and/or nickel concentrations at follow-up and cleaning status, distance from the Port, rainwater tank and roof catchment characteristics and adjusting for baseline lead or nickel concentration, were modelled using linear regression. The natural logarithms of the lead and nickel levels were used in all models because these data were skewed to the left. The dependent variable was the follow-up lead reading, with the first metal reading included in the model. Distance was measured in kilometres and as a continuous variable. Cleaning was modelled as a dichotomous variable.

The statistical analysis was conducted using STATA 9 (Texas) statistical packages [11].

#### 3. Results

#### 3.1. Descriptive Analysis of Lead and Nickel Concentrations

Among the 236 tanks randomly selected for re-sampling, 176 households agreed to have their rainwater tanks re-sampled. The median concentrations of both lead and nickel decreased between baseline and follow-up samples (Table 1). At baseline the median concentrations for lead was at the ADWG and for nickel it was above the ADWG. At follow up, the median level had reduced by 55% for lead and 85% for nickel.

Figures 2(a) and (b) present smoothed maps of lead concentrations in the study area at baseline and follow-up. Figures 3(a) and b are smoothed maps of nickel concentrations in the study area as at baseline and follow-up.

#### 3.2. Comparisons by Cleaning Status

Data on whether the rainwater tank had been cleaned were available for 161 tanks. There were reductions in

median lead and nickel concentrations in both tanks that were cleaned and those not cleaned (Table 1). The reduction was greatest for nickel in cleaned tanks. The percentage reduction in median nickel concentrations was 88%, whereas for those tanks not cleaned the reduction in nickel concentration was 63%. For lead there was little difference in the reduction between the cleaned tanks and not cleaned tanks; the reductions in the median concentrations were 58% and 60% respectively. An analysis of variance indicated that the difference in the median concentration between follow-up



Figure 2(a). Spatial distribution of lead levels in rainwater tanks at baseline, esperance March-June 2007.

Table 1. Lead and Nickel	concentrations (	( <b>mg/L</b> ) in t	tank rainwater	• at baseline	and follow-up	for all	tanks	(n=176) a	ınd by
cleaning status, Esperance	2007 (n=161)1.								

	All Ta	nks (n=176)	Tanks cleaned by Esp	PA <sup>2</sup> or privately (n=125)	Tanks not cleaned (n=36)		
Lead	Median	Range	Median	Range	Median	Range	
Baseline	0.010	0.001-0.160	0.012	0.001-0.160	0.005	0.001-0.100	
Follow up	0.004	0.0004-0.100	0.005	0.001-0.110	0.002	0.000-0.038	
Nickel							
Baseline	0.027	0.001-0.700	0.032	0.001-0.680	0.008	0.002-0.110	
Follow up	0.003	0.000-0.110	0.004	0.002-0.700	0.003	0.001-0.110	

1. cleaning status not known for 15 tanks; 2. EspPA- Esperance Port Authority.



Figure 2(b). Spatial distribution of lead levels in rainwater tanks at follow-up, Esperance, October 2007.



Figure 3(a). Spatial distribution of nickel levels in rainwater tanks at baseline, Esperance, March-June, 2007.



Figure 3(b). Spatial distribution of nickel levels in rainwater tanks at follow-up, Esperance, October 2007.

and baseline was not significantly associated with cleaning status for lead (p=0.228) but was for nickel (p<0.001).

For lead, the proportion above the ADWG reduced by 61% in the cleaned group compared with 33% in the not cleaned group. For nickel, the proportion above the ADWG reduced by 92% compared with 50% in the not cleaned group.

When the cleaned tanks were stratified by date of cleaning, that is the period, March to June, compared with July onwards, the follow up medians were the same.

#### 3.3. Characteristics of Tanks Sampled

The characteristics of the tanks and their roof and gutter catchment areas were available for maximum of 143 tanks. Tanks were predominantly made of zincalume (38%) and plastic (32%) with some colourbond (21%) and fibreglass tanks (8%). There were no concrete tanks. Nearly all tanks (96%) were reported to be in good condition. Five per cent of tanks had a first flush diverter, and most did not have an opening on the tank roof. Over half the tanks (55%) had a screened inlet.

The most common roof material was Colourbond, followed by tile. For gutters Colourbond was the most common material. Of the 132 tanks for which the roof condition was noted, 86% were in a good condition. For gutters, 44% of households cleaned their gutters at least annually, whereas 56% never or irregularly cleaned gutters.

Comparisons were made of lead and nickel concentrations at follow-up sampling by tank or roof catchment characteristics (Table 2). Opening in the tank roof was statistically significantly associated with higher nickel concentrations. While there were no significant differences in the distribution of metal concentration by tank and catchment characteristics, there was a tendency for higher lead levels to be associated with plastic tanks, tile or asbestos roofs and an opening in the tank roof. For nickel, there was a tendency for higher concentrations for colourbond roofs and gutters.

# **3.4.** Lead and Nickel Concentrations at Follow up by Distance from the Port

The distributions of lead concentrations for all 176 samples at follow up by distance from the Esperance Port are shown in Table 3. Water samples that were above the lead ADWG tended to be from tanks closer to the Port; 69.5% of samples were within 1.5 kms of the Port compared with 54% of samples below the ADWG for lead (p=0.025).

Just 13 samples were at or above the ADWG for nickel at follow-up; six of these were located within 1 km of the Port, five between 1.01 km and 1.5 km, and two were more than 2 km from the Port.

			Lead concentration				Nickel conc	entration	n
Tank and ro	of characteristics <sup>1</sup>	<0.0	01mg/L	<0.	01mg/L	<0.02mg/L		≥0.02mg/L	
		n	%	n	%	n	%	n	%
	Zincalume	43	39.1	10	33.3	48	37.8	5	38.5
Tank material	Colourbond	23	20.9	7	23.3	27	21.2	3	23.1
	Plastic	34	30.9	11	36.7	41	32.3	4	30.8
	Fibreglass	10	9.1	2	6.7	11	8.7	1	7.7
	Zincalume	19	17.3	6	20.0	23	18.1	2	15.4
Roof material	Colourbond	51	46.4	10	33.3	53	41.7	8	61.5
	Asbestos cement	6	5.4	3	10.0	7	5.5	2	15.4
	Tile	34	30.9	11	36.7	44	34.7	1	7.7
	Zincalume	32	28.3	9	30.0	39	30.0	2	15.4
<i>C u i</i> 1	Colourbond	54	47.4	16	53.3	62	47.7	8	61.5
Gutter material	Plastic	5	4.4	1	3.3	6	4.6	0	0.0
	Other	22	19.5	4	13.3	23	17.7	3	23.1
Opening in tank	No	94	83.2	24	80.0	110	84.6	8	61.5
roof <sup>2</sup>	Yes	19	16.8	6	20.0	50	15.4	5	38.5
Roof condition	Poor/average	17	16.3	1	3.6	15	12.5	3	25.0
	Good	87	83.7	27	96.4	105	87.5	9	75.0

Table 2. Cross-tabulation of tank and catchment characteristics by proportion of samples above and below 0.01mg/L lead and above and below 0.02mg/L nickel at follow up sampling (n=143).

1. Total may not add to 143 due to missing data; 2. Significant difference for nickel p=0.037.

Table 3. Lead concentrations by	v distance from	the Esperance port	(n=176).
Table 5. Leau concentrations by	y uistance nom	the Esperance por	$(\mathbf{n} - 1 / 0)$

Distance from port					
		<0.	01mg/L	≥0.0	)1mg/L
	Total	n	%	n	%
0-1.00 km	26	15	10.7	11	30.6
1.01- 1.50 km	75	61	43.6	14	38.9
1.51- 2.00km	44	38	27.1	6	16.7
More than 2.00 km	31	26	18.6	5	13.9

Table 4. Linear Regression	Models: Effect of cleaning	, distance from Port and	baseline concentration	on follow up concentra-
tion of (1) lead and (2) nick	el, (n=161).			

	Coefficient	t-statistic	95% Confide	ence Interval	P-value
Model for Lead					
Constant	-2.825	-7.35			
LnPb-Baseline	0.437	7.39	0.320	0.554	< 0.001
Cleaned versus not cleaned	0.106	0.62	-0.232	0.444	0.537
Distance in kilometres	-0.416	-3.45	-0.654	-0.177	0.001
Model for nickel					
Constant	-3.049	-9.16			
LnNi-Baseline	0.288	4.30	0.156	0.421	< 0.001
Cleaned versus not cleaned	-0.666	-3.72	-1.020	-0.312	< 0.001
Distance in kilometres	-0.569	-4.09	-0.844	-0.294	< 0.001

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#### 3.5. Linear Regression Models

Distance from the Port was significantly related to the second lead reading. As distance from the Port increases the lead concentration decreases. Cleaning status had no significant influence on the second lead reading. For nickel, both cleaning status and distance from the Port led to a significant reduction in the second nickel concentration.

None of the tank and catchment characteristics were associated with lead or nickel concentrations when included in the model (data not presented).

#### 4. Discussion

These data indicate that that there have been reductions in both lead and nickel concentrations, but that the reduction has been greater for nickel concentrations. The reduction in nickel concentration was significantly associated with cleaning status, whereas this was not the case for lead. While the lead levels in rainwater tanks have reduced, the reduction is less with increasing proximity to the Port. Tank and roof characteristics did not significantly influence the follow-up lead concentrations.

The effect of distance from the Port on follow-up lead levels may have reflected one of four possibilities. First, the Port may have been a source of ongoing lead contamination. While lead carbonate was no longer handled at the Esperance Port, the buildings, railway lines and grounds within the Port that surrounded areas where the lead carbonate was unloaded from kibbles and loaded onto ships, may have been still contaminated with lead. This lead could then have been re-entrained into the air and contaminated rainwater tanks closer to the Port. Second, trees and shrubs and soil in the local environment may still have been contaminated with lead and this lead could have been re-entrained by wind into the air and deposited on roof catchments. Investigations in Port Pirie, where a large lead-zinc smelter exists, have illustrated the persistence of higher levels of contamination nearest the smelter. Maynard el al. (2003) in a review of the Lead Decontamination Program, concluded that re-entrainment from the smelter and environs was a more important contributor to air borne lead levels than re- entrainment from contaminated areas in the city.

The winds most likely to pick up contamination from the Port and the surrounding areas and then transport this across the town site were from the North through to the South-East. During the months between the baseline and follow up samples, winds followed either an autumn or winter pattern. During autumn the prevailing winds in the morning are from the North/ North-West and North-East, and in the afternoon they are from the South-East and South. In winter period the prevailing winds were from the North-West/ North and West for both morning and afternoon (http://www.bom.gov.au/climate/averages /wind/selection\_map.shtml). Hence it is possible that rainwater tanks have been re-contaminated by lead in the environment.

Third, the cleaning protocol for rainwater required only that the bottom part of the roof (one metre) be cleaned. Cleaning of the roof catchment may not have adequately removed lead from this environment, with those closest to the Port having the higher levels of lead deposition in the past. With time this contamination would have been washed into the rainwater tanks.

Last, it may have been a combination of these and as a result a range of responses may be required. While children living closest to or downwind of the Port Pirie smelter have continued to have the highest blood lead levels, there is evidence that some interventions have been successful reducing blood lead levels in Port Pirie children [12]. These have included avoidance of tank rainwater, reduction of airborne smelter emissions, relocation of children to lower exposure suburbs, worker hygiene improvements, community education and house decontamination. While not all are relevant to Esperance, where the exposure is has a short history, is lower and no longer ongoing, a broader based intervention is required.

There are a number of reasons as to why nickel may not have re-contaminated tanks and for levels to have reduced to a greater extent than lead. Nickel has been handled at the Port for about 30 years and any cleaning of the Port environment would have removed deposits that have built up over a long period of time. The concentrate is between 8%-15% nickel, whereas for lead, the concentrate is in the order of 65% lead. There has been a number of engineering upgrades at the Port to reduce the potential for nickel dust. The EspPA has specified the minimum moisture content and pH of nickel arriving at the Port and maintained the moisture content during storage in sheds at the wharf. There has been a presence of Department of Environment and Conservation officers monitoring nickel concentrate loaded onto ships.

The extensive use of domestic rainwater collection systems across Esperance allowed us to obtain a comprehensive picture of the extent and distribution of lead and nickel contamination across the town. This would not otherwise have been obtainable in a small community such as Esperance. However, an important limitation of this study was the extent of missing data. Data were collected as part of an ongoing investigation, rather than for research purposes. While some residents had given their consent for sample collection, they were not able to be present at the time of sampling. Hence there are missing data on tank and roof characteristics as well as tank cleaning status. In other cases where surveys were administered, it was sometimes difficult for the resident, who may have been a tenant, to know or recall information on tank and roof characteristics.

In conclusion, the most important factor influencing the follow-up lead readings was the distance from the Port. As the distance from the Port increased, the follow-up lead concentration decreased. On the other hand, whether a tank was cleaned had no apparent effect on the follow-up lead concentration. These findings suggest that there may be ongoing contamination of rainwater tanks from the environment. The pattern of continuing high lead levels may be a result of ongoing contamination arising from the Port environment, the re-mobilisation of existing lead contamination of the environment, the difficulties in removing residual lead from the roof catchment areas or a combination of these. Nickel levels have been reduced substantially as a result of the rainwater tank cleaning program.

As a result of these findings it was recommended that people in Esperance continue to be advised not to drink rainwater. In addition, it was recommended that there be further investigation of lead levels in the Port environs, the surrounding residential areas and roofs to identify and address any environmental sources of lead.

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# Study on Ecological Compensation Policy among the Micro Subjects on Water Energy Resources Development

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### Abstract

The subjects of ecological compensation involve the nation, society, development enterprises of water-energy resources, as well as the location of resource itself. This paper systematically studies on how to make "water energy sources market compensation policy", "the economic compensation policy for relevant interest subjects" and "the ecological compensation policy of basin ecological water." So, it is necessary to exert the complementary function between market compensation and government compensation by the means of economic compensation and to establish the ecological compensation policy of basin ecological water, which is beneficial to coordinating the stakeholders' interests of cross-region or inter-basin. And it is important and significant to establish constantly perfected ecological compensation policy among the micro subjects on water energy resources development, so as to coordinate interest relationships among various subjects and finally reach the aim of sustainable use of water energy resources and environmental protection as possible.

Keywords: Ecological Compensation Policy, Water Energy Resources Development, Micro Subjects, Resource Compensation, Economic Compensation, Regional Ecological Water, Market Compensation, Government Compensation

### 1. Introduction

Ecological compensation is an institutional arrangement regulating interests relation of relevant persons chiefly by economic means for the purpose of protecting and utilizing ecosystem services sustainably. [1] The subjects of ecological compensation include the nation, society, development enterprises of water-energy resources, as well as the location of resource itself. The concrete can be divided into the following categories: state compensation, society compensation and self-compensation. In the exploration of water energy resources, the relevant subjects of interests involve developers of resources, the contemporary interest subjects and the descendant interest subjects. Due to no spokesman for future generations, the responsibilities will naturally fall on the state on behalf of the interests of the descendant interest subjects. Therefore, the internal mechanism of policy analysis is mainly related to the compensation of the hydropower resources for the sustainable use of resources, the economic compensation for the contemporary interest subjects and the ecological environmental compensation for the descendant interest subjects. In China, researches on eco-compensation mainly focuses on forestry [2], "conversion of cropland to forest" [3] and "returning farmland to lake" [4], mineral resource utilization[5], ecocompensation for the regional development [6,7], the compensation mechanism under various policies [8] and so on. With regard to the eco-compensation mechanism of water energy resources development and utilization, the study centers on the compensation policy, including compensation and compensation mechanism of hydraulic engineering [9], the sustainable use of hydropower resources, hydropower market standardization [10,11] and so on. These researches are all having made certain contributions to China's ecological protection in different perspectives. This paper gives comparatively systematic researches on the three ecological compensation policies



of water energy resources development: resource market compensation; economic compensation; basin ecological water. It may serve as references for the governmental bodies and other social public departments to institute environmental policies, as well as for the stakeholders to solve or coordinate the interest relationships in the water energy resource development. So it will be important theoretically and practically to strengthen this research field, so as to coordinate the interest relationships among micro-subjects, sustainably utilize water energy resources and finally reach the aim of ecological protection as possible.

### 2. Resource Market Compensation Policy for Water Energy Resources

Although it is clearly stipulated in Water Law of PRC that "water resources belong to the state", and "the state carries out water abstraction licensing and paid use of water resources", there is no specific regulations and implementing method for the management of developing and using right for water energy resources. In order to balance the interests among the country, investors and residents and reduce economic losses in water energy resource development, the government should enact the laws and regulations about occupation and utilization of scarce resources, so as to form an opportunity for fair competition as far as possible, rather than the special right for only some enterprises and individuals. It is just by market rules that ecological compensation mechanism becomes one of the best way to rationally settle the relationships among environmental protection, benefits and damages. [12] By market competition mechanism, more and more enterprises can take part in the competition or cooperation of water energy resource development.

# 2.1. Exert the Roles of Market Mechanism in Water Energy Resources Development

In general, there are two forms of compensable transfer of hydropower resources. One is negotiating transfer, which happens only when a few investors take part in the competition. The other is a number of investors for the right to development, the situation when many investors scramble for the right of resource development. The most efficient way is to deploy resources through the mechanism of market competition. That is by public auction to decide the developers. So it is necessary to establish trading market of property rights among the property right subject. In order to obtain the property rights of environmental resource development, transaction subjects will bid against each other, and finally the property right blogs to the highest bidder. The high costs of property rights of environmental resources will inevitably encourage the subject to effectively use and protect the rights, so as to avoid operation of low efficiency and the "external diseconomy" caused by the monopoly of environmental resources property. [13] The fundamental goal of the ecological compensation policy, which involves numerous stakeholders, is to regulate the economic interests of protectors in ecological security. However, in current policy-making process of ecological protection, there is still lack of extensive participation mechanism of stakeholders. Moreover, the current policies embody the will of central government much more than the stakeholders' interests of local government and ecological protection area, which may be divorced from reality and not good for environmental protection. The market compensation, a way of market incentive, includes "pollution charge", "the exchange of environmental property right", "environmental protection fund", "environmental liability insurance", "contract compensation of environmental protection industry", and so on. It is just by the above way that the market mechanism in water energy resources development can embody, as much as possible, the market value of the ecological resources under the government's macro-control. In addition, the diversification of market subjects of environmental property rights will be beneficial to embodying the real value of resources through price lever transferring among various subjects. [14]

#### 2.2. Deal Well with the Relationships between Market Compensation and Government Compensation

Certainly, market compensation in the scope of government regulation and control endows the ecological resources with the commodity attributes through the market mechanism, in which the cost of the ecological environment will be incorporated into the subject decision- making so as to make the developer and user of eco-environmental resources bear the corresponding responsibility. Comparing with the government compensation, the market compensation possesses the following shortcomings: the difficulty of compensation; serious short-term behavior for compensation; the lack of relevant laws and regulations. [15] For example [10,11,16], as per the experience of Zhejiang province, to set up an open, fair and just market mechanism of transfer of resources, attention must be paid as the following aspects:

- Before a transfer of resources, the governments do a good plan and master the status of the intra-regional resources. According to the size of the investment, disclosure of information should be issued in the corresponding span of the media, and barriers to entry should be broken in huge investment.
- As for water resources development projects of the comprehensive utilization, in particular, the project

with flood control and drainage and other social public welfare projects with functions of flood control and drainage, the results of the auction may make the price of developing right "negative". That means national finance needs to put money to investors. In fact, the government's investment plus the transfer price of resources is just equal to the investment of other public welfare projects except the function of power generation. This part should be invested by the government. The "negative" price does not contradict the theory in the market allocation of scarce resources.

- When there are not enough participants in a public auction, the two sides adopt transfer mechanism of the agreement, but a certain amount of resource prices must be reflected. Fundamentally, the possible legal disputes resulting from historical development will be eliminated as possible.
- When the government intends to support investors, it can take the form of resource stock, but the stock right belongs to the state instead of the local residents.

At the initial stage of ecological compensation, it is necessary to exert the guiding function of the government in the process of the establishment of an ecological compensation mechanism, and to improve the input mechanism of public finance for ecological protection. Meanwhile, the multilateral financing channel and market-oriented operation way should be established based on the policies and regulations standardizing and restraining the behavior of the subjects of market economy.

### 3. The Economic Compensation Policy for Relevant Interest Subjects

Although the water energy resources and land resources belong to the country, local residents have the right to use. If the process of water energy resources development involves the problems such as emigration, land expropriation and so on, investors should give financial compensation for local residents. This inevitably involves external problem during the development of hydropower resources. The externality of water energy resources development and utilization refers to the local social, economic and environmental effects caused by the subjects of hydropower construction which will lead to the increase of the cost or benefit. [17] The direction and result of externality show the dual nature, namely "external economy" and "external diseconomies". Those which are able to bring about benefits or the reduction of costs for the society or individuals are called "external economy", while those which are able to decrease the benefits or increase the costs for the society or individuals are called "external diseconomy" or "market failure" [11].

#### 3.1. Establish a Macro-Level Hydropower Resources Compensation Mechanism

The compensation mechanism of water energy resources development should be based on the principle of the combination of government regulation and voluntary negotiation. The negative externality of water resources allocation involves three levels. The first level is state in macro-scope. The adjustment of general planning for the whole watershed will make some people damage or benefit. In order to guarantee mass benefit and social stability and protect ecological environment in the reservoir region and its downstream regions, measures of aftercare and compensation should be carried out according to existing laws and regulations as well as policy. These mandatory measures and compensation criterion should be stipulated by state and government. The state should make the ecologic flux of channel, volume standard of water environment, guarantee measures of the minimum water demand per capita and so on.

#### 3.2. Establish Ecological Compensation Mechanism of Water Resources Property Right

The definition of property right is precondition of compensation mechanism. It is only the clear property right that can determine externality, and the compensation mechanism can come true. But in China, the concept of "water right" was put forward for not a long time. The property rights of water resources should includes ownership, administrative power, use right and management right. The ownership of water resources belongs to the state; the administrative power of water resources belongs to the government; the management right belongs to enterprises. The use right includes the most fundamental use right of residents along the river except for use right obtained by enterprises. Therefore, the income by auction of hydropower resources and negotiating transfer, except the compensation for the state-owned right of water resources, includes the compensation of local residents related to basin water resources.

#### 3.3. Establish a Micro-Level Hydropower Resources Compensation Mechanism

Because the development of water energy resources affects the interests of other economic subject, such condition belongs to category of micro economy. Thus the compensation measures and standard should be achieved by bilateral negotiation as per severity of influence. At this stage, the negative externality of water resources development should include two levels: There are clear externalities in the feasibility study phase of hydropower resource development; or there are no clear externalities in the feasibility study phase, but accidental occurrence of negative externalities in the operation after water resource development.

### 3.4. Establish Compensation Mechanism for External Economy

The water energy resources development have a positive economic, ecological and social benefits, including the construction of hydropower stations in remote mountain areas without electricity, raising the standard of flood control in the downstream channel of a hydroelectric station, reducing environmental pollution caused by fuel for power generation, construction of reservoirs guaranteeing the domestic water and the process water of downstream residents, etc. These are properties of quasi-public goods. The state should adopt the mechanism of policy compensation or market compensation. The policy compensation mainly settles the problem of no electricity in remote mountainous areas; enhance the standard of the downstream of the hydropower stations, take measures of cash subsidy or discount interest loan to reduce investors' costs. The market mechanism is taken to reduce the environmental pollution resulting from fuel for power generation. It can be implemented by the way of pollution emission indexes and quota system on clean energy. The power stations may transact pollution-emission indexes through market indicators, and the hydropower stations may transfer clean-energy quota to the power plants through market.

# 3.5. Regulate the Decision-Making Mechanism of Grassroots-Level Governments

The major externality of water energy resource development is the effect of public living using of water and water environment change. In the principle of collective will, the policy scheme should be dealt with on the basis of the decision-making of village committee through discussion and vote of the villagers' representative. However, a lot of the village committees have no administrative authority at all, let alone the exertion of public power. Therefore, it is necessary to regulate the decision-making mechanism of grassroots-level governments, so as to ensure the necessary administrative expenditures of village collective, condense feelings of the village-level cadres, resolve conflicts between investors and villagers.

# 4. The Ecological Compensation Policy of Basin Ecological Water

Ecological compensation of basin water refers to "The government and favored area of lower reaches give economic compensation for ecological benefit created by upper reaches", that is to say "In order to restore, maintain and enhance the ecological function of the ecological system, the external economy will be increased by compensating for the behavior conducive to the ecological service from the upstream area, so as to reach the aim of protection and improvement of water eco-environment." [16] The ecological compensation system is carried out primarily by setting ecological flows. In the process of water energy resources development, it inevitably causes zero flow of local rivers and change of river flow, which is related to the current development mode and cannot be eliminated. It is through eco-compensation that can minimize the environmental effects as possible.

# 4.1. Establish Effective Reward Institution of Water Right

After completion of hydropower station, the flow in the rivers of mountain can be controlled through engineering measures and ecological self-rehabilitation. The flow of channel in the specific dry season changes in right direction to improve the state of the natural water flow. Concrete measures include as follows: The government compulsorily determines the ecological flow and ensures the implementation of ecological engineering measures, rules and regulations. On the other hand, through negotiated contract, the above aim can be reached too. Mandatory ecological flow compensation plus consultative compensation flow equals to improvement of the ecological environment. In 2001, the Yiwu city and the Dongyang city, located in the upstream and downstream of Jinhuajiang river in Zhejiang province, signed a water-right transferring agreement, which become China's first case of water rights transactions through market mechanism.[16] The Dongyang city transferred the permanent use-right of Hengjin reservoir of 50,000,000 m<sup>3</sup> to the Yiwu City at the price of RMB 4 yuan per m<sup>3</sup>. So the Yiwu City invests 200 million yuan one time to purchase the right to use, while the original ownership unchanged, and the Yiwu city paid comprehensive management-fees at RMB 0.1yuan per m<sup>3</sup> according to the actual current-year water supply.

# 4.2. Establish Unified System of Configuration of Basin Water Resources

The scheduling right is clear about reservoir of state power plant in flood period. Water level control must obey the dispatch of water or flood control department. As for the hydropower station reservoir carrying out compensable transfer, since the use rights was defined as private property rights, the actual treatment will be different. But the basic principle is that the private interests should be subject to public interest when human right of life is under threat. The water resources property right, regardless of public ownership or private property right must accept the nation's dispatch. Such systems should acquire the promise in the initial transfer contract of water rights. As to water consumption of environment, during the drought dry season, it is particularly important for government to posses the dispatching right of reservoir. Only in this way, should the water consumption of ecological environment be improved.

# 4.3. Study and Determine the Minimum Ecological Flow

The significance of minimum ecological flow is to maintain the continuity of the river, which is the necessary condition for the effective maintenance of river morphology and is favorable for some of the aquatic organisms to adapt to the adverse ecological environment in the dry season as soon as possible. Once below this flow, the river will face the danger of cutoff or dry up, and the self-survival function of the river will be damaged. [18] Therefore, it is very important to research on minimum ecological flow, which is beneficial to maintaining the integrity of the river of the lower reaches of the river and restoring its unique function and ecological security. [19] Ecological flow is a range of value including the maximum ecological flow and minimum ecological flow. Because the construction of hydropower stations in general can reduce the negative impact of the floods, control water flow, and have a positive externality, which makes allocation of water resources conduce to the achievement of Qmin-Qmax. Owing to less water coming during the dry season, the construction of hydropower stations will aggravate the scarcity of water resources. So the river flow will be less than Qmin away from the range of Qmin-Qmax. In such a way, the ecological crisis of channel will happen. For example [18], based on the viewpoint of maintenance of the critical survival condition of river water and characteristics of geomorphology of control sections of different channels of the Liaohe River, the rates of minimum ecological discharge of the river channels were calculated and their characteristics were analyzed from the aspect of water quantity, which is the most fundamental factor of ecological water demand. As a result, the control criterion for minimum discharge of the Liaohe River was deduced.

#### 4.4. Establish Contract Mechanism between Enterprise and Representative of Ecological Interests

As the above has established the specific ecological river flow, at this stage, the future operation mode of the reservoir should be set. That is to make the future specific mode of water discharge under certain conditions. For example, in the southern area, it is not necessary to input the ecological flow in the rain-abundant spring. On the contrary, in the rain-scarce summer, much more water flow should be input. In the contract, one signing party is the hydropower plant; the other is the management departments of the river or the chief representatives of the downstream villagers. Furthermore, the requirements of water quality and water quantity of different river reaches, which is the core of the basin water ecological compensation [20], must be clarified in the contract, and meanwhile the compensation responsibility with or without reaching the standards must be defined clearly, too.

### 5. Conclusions

Ecological compensation mechanism, through adjusting the relationship of relevant groups between environment and economic benefits, encourages ecological environmental protection, and promotes equity and development between regions and social groups. China's current system of water resources management has certain gaps with the requirements of sustainable use of water resources. Meanwhile, the management system of water energy resources is directly related to the management system of water resources. At present, among the subjects of water resources allocation in China, there are too many interest subjects exercising administrative functions on behalf of the government's interests, such as environmental protection departments, plans, water conservancy, urban construction, land, forestry and other departments. Thus, it is necessary to integrate watermanagement functions of various government- departments, and establish a scientific and efficient watermanagement system, so as to clearly define the interest subject "the state". Although water energy resources management is an integral part of water resources management, the undefined management responsibility of water energy is the main problem in the water energy resources management currently. On the basis of practical experience, the water energy resources management should be brought into the category of water resources management. The water energy resources management mechanism of unified management and graded responsibility should be established at the national level. The right of planning, use and development should be defined clearly to guarantee the specification, the orderliness and rational development. So, it is important to exert the complementary function between market compensation and government compensation by the means of economic compensation, and to establish the ecological compensation policy of basin ecological water, which is beneficial to coordinating the stakeholders' interests of cross-region or inter-basin. No matter what kind of policy, it is a constantly perfected process, which will induce us to explore and study continuously it.

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# **Preparation of Nanoiron by Water-in-Oil (W/O) Microemulsion for Reduction of Nitrate in Groundwater**

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### Abstract

Nanometer-sized iron particles with monodispersity and narrow size distribution were synthesized by modified microemulsion system using environment-friendly non-ionic surfactants Span 80 and Tween 60 as mixed surfactants. The synthesized iron nanoparticles were characterized by using powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). The results show that the synthesized particles were mainly composed of  $\alpha$ -Fe with an average diameter of 80–90 nm. The chemical activity of the obtained iron nanoparticles was evaluated by the denitrification of nitrate in water. On neutral condition, complete denitrification of nitrate was achieved by freshly synthesized nanoiron within 30 min. Ammonia was the main product, with good material balance at the end of the reaction. Two possible reaction pathways for nitrate reduction by nanoiron have been proposed in this study.

Keywords: Iron Nanoparticles, Microemulsion, Reduction, Nitrate

## 1. Introduction

Metallic nanoparticles play important roles in many different areas by virtue of their unique microstructure (small size effect, quantum effect, and surface effect). The physical and chemical properties of the nanoparticles are different from those of bulk metal due to their extremely small sizes and large specific surface areas. They have been widely used in the areas of catalysis, luminous materials, high quality magnetic materials, electronics, biomedical engineering and environmental remediation [1–4]. Recently, the use of nanoscale materials for in-situ remediation of non-aqueous phase liquids (NAPLs) [5–7] and heavy metals (e.g. As, Cr, and Pb) [8,9] in groundwater has been deeply and extensively studied, and much progress has been achieved.

Water-in-oil (W/O) microemulsions or reverse micelles, which are also called intelligent microreactors [10,11], are of particular interest in fabricating nanoparticles. The W/O microemulsions consist of nanosized water droplets that are dispersed in a continuous oil medium and stabilized by surfactant mole-

cules accumulated at the oil/water interface. A variety of reactants can be introduced into nanosized water droplets for reactions confined within the microreactors, leading to materials with uniform size. The highly dispersed water pools are ideal nanostructured reaction media for producing non-agglomerate and monodispersed nanoparticles. The synthesized nanoparticles can be stably preserved in the microemulsion system for a long time [12–14].

In this study, the environmental-friendly surfactants sorbitan monooleate (Span 80) and polyoxyethylene (20) sorbitan monostearate (Tween 60) were chosen as mixed surfactants. The water solubilization capacity and the properties of the water molecules solubilized in the interior of the S-T/isooctane system were investigated in order to prepare a transparent, isotropic, and thermodynamically stable W/O microemulsion system and then the reverse micelles were used as nanoreactors to synthesize iron nanoparticles, which can be used in environmental contaminants remediation. The properties of the synthetic iron nanoparticles were characterized and analyzed.



### 2. Experiments

#### 2.1. Materials and Methods

Span 80 (chemical grade), Tween 60 (chemical grade), potassium borohydride (KBH<sub>4</sub>, analytical grade), ferrous sulfate heptahydrate (FeSO<sub>4</sub>•7H<sub>2</sub>O, analytical grade) were purchased from Fuchen Chemical Reagent Manufactory Tianjin, China. n-Butanol (analytical grade) and isooctane (analytical grade) were supplied by the Sixth Chemical Reagent Manufactory (Tianjin, China) and Kaitong Chemical Reagents Ltd. (Tianjin, China), respectively. All the chemicals were used without further purification. Deionized water was used for aqueous solution and washing in this study.

Morphologies and sizes of the particles were observed with a Philips EM400ST TEM (transmission electron microscopy) (Eindhoven, Netherlands). Crystal structures of the final products were examined with a Rigaku D/max-2500 XRD (X-ray diffraction) (Tokyo, Japan), with Cu-Ka radiation, voltage was set at 40 kV, and current was 100 mA (k=0.1541nm). The conductivity was measured with a microprocessor conductometer (DDS-307, Shanghai Precision and Scientific Instrument Corporation, Shanghai, China). The concentrations of nitrate, nitrite, and ammonium were measured colorimetrically according to the methods 4,500 listed in the 20th edition of the Standard Methods using a UV-Vis spectrophotometer (752N Ultraviolet/Visible Spectrometer, Shanghai Precision and Scientific Instrument Corporation, Shanghai, China) [15].

#### 2.2. Preparation of Water/Mixed Surfactants/ Isooctane Microemulsion

Mixed surfactants with different hydrophilic-lipophilic balance (HLB) value were prepared by Span 80 and Tween 60. A given amount of mixed surfactants were mixed with a certain amount of isooctane at a fixed weight ratio, and then dispersed by ultrasound for several minutes. A certain amount of n-butanol used as cosurfactants was added to the above mixture. The conductivity of the system was measured after being dispersed by ultrasound. Deionized water was gradually added into the system by a micro-burette, and the formation of the optically clear microemulsion was determined by conductivity measurement and visual examination.

#### 2.3. Preparation of Nanoscale Iron

The iron nanoparticles were formed from the following reaction

 $Fe^{2+}+2BH_4^-+6H_2O \rightarrow Fe+2B(OH)_3+7H_2\uparrow$ 

Two water/S-T (Span-Tween mixed surfactants)/ isooctane microemulsions, A and B, differing only in the types of aqueous phase, were prepared. The microemulsions were both composed of 2.0 g S-T (Span-Tween mixed surfactants) mixed surfactant, 4.0 g isooctane, 1.0 g n-butanol, and 2 mL aqueous solution. The aqueous phase of microemulsion A was 0.2 mol/L FeSO<sub>4</sub> solution, whereas the aqueous phase of microemulsion B was 1.3 mol/L KBH<sub>4</sub> solutions. Microemulsions A and B were quickly mixed under the protection of argon in a conical flask. The solution turned black after mixing, and was allowed to react for 30 min with vigorous stirring (3,000r/min). At the end of the reaction, the microemulsion system with the well-dispersed iron nanoparticles was transferred into a sealed vessel filled with argon by a double-tipped needle. The resulting black-gray solids were settled by magnet, and the supernatant was decanted. Then the solids were washed with deionized water and finally with a mixture of anhydrous ethanol and acetone (volumetric ratio of ethanol and acetone was 1:1) for six times, respectively. Finally, the resultant blackgray solids were dried under argon atmosphere, and then stored in another sealed vessel filled with argon.

#### 2.4. Characterization of Particles

A small amount of microemulsion containing the iron particles were withdrawn from the reaction vessel, and then preserved in a small sealed glass tube. For the TEM investigations, a small drop of microemulsion containing iron nanoparticles was deposited on a copper grid.

The black precipitates formed in the microemulsion were washed with anhydrous ethanol/acetone (volumetric ratio of ethanol and acetone is 1:1) several times and then with deoxygenated and deionized water and finally dried. The entire operation was carried out under an atmosphere of argon. The final dry black solids were analyzed by XRD.

#### 2.5. Reactivity Assessment

The performance of the synthetic iron nanoparticles was tested by the reduction of nitrate under anaerobic condition. The synthesized iron nanoparticles react with 80 mg/L nitrate solution at initial neutral condition under ambient temperature without pH control. The concentrations of nitrate were periodically analyzed by ultraviolet (UV) (using Standard Methods) [15].

#### 3. Results and Discussion

#### **3.1.** Orthogonal Experiments

The results of orthogonal experiments indicated that the optimum conditions for the formation of microemulsion system are: hydrophilic-lipophilic balance (HLB) was 14,

weight ratio of oil and surfactants was 2, and weight ratio of cosurfactants and surfactants was 0.5.

#### 3.2. Phase Behavior of Water/Mixed Surfactants/ Isooctane Microemulsion System

In order to construct the phase diagram of the water/mixed surfactants/isooctane microemulsion system, the titration method was used. The optimum weight ratio mentioned above was used to prepare the mixed surfactants/n-butanol mixture (SAA-Co). A predetermined amount of isooctane was added to the surfactant mixture. Water was then added into the isooctane/surfactant mixture and changes were observed by visual inspection and conductivity measurement and the information was used to develop a phase diagram. The phase behavior of the water/mixed surfactants/isooctane system is shown in Figure 1. It can be seen in Figure 1 that an ideal W/O region has been observed where weight ratio of n-butanol and mixed surfactants was 1:2, which will be used as the microemulsion system to produce nanoiron particles.

#### 3.3. Conductivity

The variation of conductivity with different water content (v) is shown in Figure 2. Two turning points (R1, R2) are found in Figure 2. Almost no change was observed in the initial conductivity of the isooctane/surfactant mixture when v was smaller than 15% (R1). This was attributed to the formation of surfactant-bonded water [16] in the system. However, the conductivity increased sharply when v was bigger than 25% (R2) upon addition of the water into the isooctane/surfactant mixture for it formed water-in-oil (W/O) microemulsion. In this region, water was present in micelle form and the size and number of water droplets increased with an increased amount of



Figure 1. Microemulsion phase diagram of Span80/ Tween60-Isooctane-H<sub>2</sub>O system.

water. When the droplet size increased, it was easy to exchange charges between the droplets, and hence the conductivity increased. The conductivity reached the maximum when the water content was 25% (wt%,R2). This can be explained by the saturation of droplets and the percolation of charges through the droplet clusters with the minimum resistance. The more water was added to the system when v was bigger than 25% (R2), the more phase separation and the conductivity decreased. The optically clear W/O microemulsion system that was formed between R1 and R2 can be used as microreactors for preparation of nanoscale iron.

#### **3.4.** Characterization of the Products by Transmission Electron Microscopy

Morphologies of the particles are shown in Figure 3(a)–(f). Figure 3(a) reveals that the synthesized iron nanoparticles dispersed well in the microemulsion system. It can be seen from the TEM images in Figure 3(b) and (c) that the particles were nearly spherical in shape and uniform in size. Figure 3(d) shows clearly the morphology and inner structure of an individual nanoparticle. Apparently, there are two distinct layers as a core-shell -like structure, where the light black and gray shell (thickness of about 10 nm) is probably due to S-T mixture while the core with the thickness of about 80–90 nm is attributed to Fe<sup>0</sup>.

Comparing Figure 3(e) with (f), the iron nanoparticles were not so well-dispersed after breakdown of the microemulsion by washing. The individual small iron nanoparticles aggregate to significantly larger nanoparticles after being separated from the "water pools", and had an irregularly spherical shape. This is because that the S-T mixture shell was destroyed in the washing procedure, and thus the mobility of particles increased.



Figure 2. Variation of conductivity with amount of water in microemulsion.



Figure 3. TEM images of Fe ultrafine particles (a), (b), (c), (d) Iron particles before demulsification; (e), (f) iron particles after demulsification.

#### 3.5. X-Ray Diffraction Results

Figure 4 is the X-ray diffraction pattern of nanoiron and shows that crystal iron particles existed in the product. The XRD pattern shows characteristic broad peaks, which is consistent with the  $\alpha$ -Fe standard pattern in the range of 20°–80°; and therefore, it is concluded that the nanoiron synthesized in this work was mainly composed of  $\alpha$ -Fe.

#### 3.6. Results of Reactivity Assessments

The reaction between nanoiron and nitrate was used to evaluate the reactivity of the synthesized iron nanoparticles. Freshly synthesized iron nanoparticles (0.25g) were charged into 125 mL solution containing 80 mg/L nitrate which was prepared in the laboratory. The black iron nanoparticles were quickly solubilized (the system turned reddish-brown when there is oxygen in it), which indicated that the freshly synthesized iron nanoparticles reacted instantly with oxidative matters in the solution. Freshly synthesized iron nanoparticles reacted with nitrate much faster than reduced Fe<sup>0</sup> powder under the same condition. On neutral condition, commercially available Fe<sup>0</sup> powder did not react with nitrate in 120 min, whereas complete denitrification of nitrate was achieved by freshly synthesized nanoiron in 30 min (Figure 5). A smaller particle size and much higher specific surface area of nanosized zero-valent iron as compared with the reduced  $Fe^0$  powder should account for the high reduction rate for nitrate by nanoscale iron used in this study. Compared with microscale particles, the superficial atom ratio of nanoscale particles dramatically increased from 1%–2% to more than 50%, resulting in greatly increased chemical reactivity, high specific surface area, and superior surface reactivity. Thus, nanoscale iron contacted and reacted more easily with contaminants than general  $Fe^0$  powder.

#### 3.7. Proposed Reaction Pathways

Figure 6 reveals that ammonia was the predominant endproduct of the reaction between nanoscale iron and nitrate. Only small amounts of nitrite were detected in the reaction process, and rapid transformation to ammonia was observed subsequently. It can be seen from the chemical mass balance curve that total nitrogen (sum of nitrate, nitrite, and ammonia) displayed a minor dip at the initial stage (from 0 to 10 min) of nitrate reduction, indicating that the reaction mechanisms were complex.



Figure 4. X-ray diffraction (XRD) pattern of Fe ultrafine particles.



Figure 5. Reactions of nitrate with commercial Fe powders (Fe), nanoscale Fe particles (nano Fe) at pH 7.

Therefore, two possible reaction pathways were proposed for nitrate reduction by nanoscale zero-valent iron as shown in Figure 7: 1) directly reduce to ammonia and 2) first adsorb to the nanoiron surface and then reduce to ammonia. The adsorption of nitrate onto nanoiron surface resulted in total nitrogen (in aqueous solution) decreasing at first. However, the amount of nitrate which adsorbed to the nanoiron surface was rapidly reduced to ammonia, and then desorbed into the solution from iron surface again, so total nitrogen in the solution increased nearly to the initial level at the end of the reaction. So, the reaction pathway of nitrate reduction by nanorion is the second one.

#### 3.8. Reaction Kinetics of Nitrate

To study the kinetics of denitrification by nanoscale iron, the effect of nitrate concentrations on the nitrate removal rate was observed. Four different initial nitrate concentrations (30,50,80,120 mg/l) were tried and the changes in nitrate concentrations with reaction time are given in Figure 8. For avoiding the effect of changes of  $Fe^{0}$  concentration by corrosion on the kinetics during the reaction, stoichiometric excess of  $Fe^{0}$  particles compared with nitrate applied were added.



Figure 6. Mass balance of nitrate reduction with nanoscale Fe.



Figure 7. Pathways of nitrate reduction by nanoscale Fe.



Figure 8. Reaction of nanoscale iron particles with different initial  $NO_3$ -N concentration solution.



Figure 9. Plot of lnr-lnC under different initial NO<sub>3</sub><sup>-</sup>N concentration.

Table 1. Reaction rate equation for reduction of nitrate having different initial concentrations by nanoscale ZVI.

Initial conc. of nitrate mg-N/L	Reaction order n	$K_{obs}$ (mg-N/L) <sup>1-n</sup> ·min <sup>-1</sup>	R
30	0.26	1.08	0.9986
50	0.54	0.55	0.9995
80	0.66	0.41	0.9997
120	0.54	0.54	0.9496

Excluding the effect of iron concentration, the reaction can be described as follows:

$$r = \frac{-dC}{dt} = k_{obs}C^{n}$$
  
ln  $r = \ln(\frac{-dC}{dt}) = \ln(k_{obs} \cdot C^{n}) = \ln k_{obs} + n \ln C$ 

where r is reaction rate,  $k_{obs}$  is the observed reaction rate constant, n is reaction orders. Plot the ln  $k_{obs}$  values vs lnr. The good fit of the linear model to data was observed from Figure 9. And, the slopes of these lines result in apparent reaction orders. The values of n were observed in Table 1. Furthermore, the same result was also observed in other studies of chemical reduction of nitrate by nanosized iron [16].

#### 4. Acknowledgment

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# **Study on the Heavy Metals Removal Efficiencies of Constructed Wetlands with Different Substrates**

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#### Abstract

In this study constructed wetlands (CWs) were used to remove three heavy metals (Zn, Cu and Pb). The two tested substrates were made of coke and gravel, respectively. First order dynamic model was appropriate to describe removing of Zn and Cu. The experimental results showed that first dynamic removal rate constants of Zn in CWs with coke and gravel were  $0.2326 \text{ h}^{-1}$  and  $0.1222 \text{ h}^{-1}$ , respectively. And those of Cu in CWs with coke and gravel were  $0.2017 \text{ h}^{-1}$  and  $0.3739 \text{ h}^{-1}$ . However, removal efficiencies of Pb in the coke system and the gravel system were within 95–99%, so the first order dynamic model failed to fit the experimental data because the hydraulic resident times of Pb did not affect outlet concentration of Pb. From the removal rate constants, it is found that the coke and gravel system have different absorption efficiencies of heavy metal pollutants. Therefore, it is suggested that the removal efficiencies of heavy metals are influenced by the choice of substrates to some extent.

Keywords: Subsurface Flow Constructed Wetlands, First Order Dynamic Model, Heavy Metal Pollutant, Substrate, Removal Efficiency

### 1. Introduction

Constructed wetlands have the characteristics of excellent performance, minimal investment and operating cost, remarkable economical and social benefits in treating wastewater. In the past 30 years, Europe and North America had set up several thousand constructed wetlands, but the designs and the operations of CWs are mostly based on statistical data and the empirical formula. However, the removal mechanism of pollutants [1] is important bases of the engineering designs of the CWs, and can provide reliability of CWs in engineering design and operation.

There are a number of physical, chemical and (micro) biological processes in purification, like sedimentation, filtration, adsorption, microbial decomposition and chemical transformation [2]. Adsorption may play an important role in the removal process. Consequently, it is important to select those substrates of high ecological activity and adsorption capacity. There has been some recent work that has attempted to investigate the influence of different substrates [3,4]. But those researches

mainly focus on the treatment of wastewater containing P and N. There remains a lack of information on heavy metals purification effects in the CWs systems with different substrates.

The aim of this present study was to investigate the removing dynamics of three heavy metal pollutant in CWs with two substrates. Since the coke and gravel differs in their porosity, their purification efficiency may be different. In the present study two CWs (coke and gravel) were set up. The effluent was collected and analyzed for heavy metal concentrations.

With the development of the China industry, heavy metal pollution became more and more serious. Base on the investigation of Yangtze River, the best quality river of the seven rivers in China, heavy metals especially Zn, Pb, Cu and Cr had polluted the water systems [5]. Considering amount of waste water containing Zn, Pb and Cu mainly discharged by steel plants and copper metallurgy plants, the water pollution on Pb, Zn and Cu were studied in this paper.

Plant plays an important role in CWs. Plant root zone and substrate absorb ionic heavy metal. We aimed to



provide more data about the purification effects of CWs with different substrates. In the present study, the different heavy metals contents absorbed by plant were determined after CWs run a long time, and then the role of plant in CWs were analyzed. Finally, it is hoped that the question of stability in root zone and substrate absorption will be resolved.

The first order dynamic model, which was used to predict the removal efficiencies of the pollutants treated by CWs, should be used in the design of the CWs [2,6–8]. Though the parameter and the calculation of the equation are simple, first order dynamic model has some limitations. However it is still an appropriate equation for describing the removal mechanism of the CWs treating pollutants. In the present study, the first order model with two parameters was used to describe the removal mechanism of the different CWs.

If steady and plug flow conditions are assumed, first order dynamic model can be used to describe the reduction of pollutants. The equation can be written as:

$$\frac{dC}{dt} = -k_v \times C \tag{1}$$

$$\frac{dC}{dx} = -\frac{k}{q} \times C \tag{2}$$

where *C* is the concentration of the quantity concerned (mg/L), *t* is the hydraulic resident time (h),  $k_v$  is volumetric rate constant (h<sup>-1</sup>), *x* is the fraction of the distance through the wetland, *k* is the areal rate constant (m/h), and *q* is the hydraulic loading rate (m/h).

The rate constant always has two expression ways $k_{v}$  and k. Literature is available on  $k_{v}$  with subsurface flow constructed wetland and k with surface flow constructed wetland [9]. Removal rate constant represents the removal ability of the CWs. In theory, the removal rate constant relates to temperature, medium (the amount and types of microorganisms) and pollutants. Therefore, in this study the temperature was kept between  $25^{\circ}$ C- $30^{\circ}$ C and the removal efficiencies of three type heavy metal pollutants (Zn, Cu and Pb) were analyzed. For the microbial membranes on the substrates were pitchy and dense, we believed the microbial membranes were steady and the microorganism were adapted to system environment. In order to compare the removal ability of different subsurface flow constructed wetlands, we established this study to determine the volumetric rate constant,  $k_{\nu}$ .

Even though there are non-degradable material in CWs, atmospheric and groundwater chemical additions, chemical speciation, and the biogeochemical cycle may generate background concentrations. Kadlec and Knight proposed a two-parameter model to describe the reduction of pollutants [2]. The equation can be written as:

$$\frac{dC}{dt} = -k_v (C - C^*) \tag{3}$$

where  $C^*$  is the background concentration.

The key to a quantitative model of wetland operation is the determination of the volumetric rate constant,  $k_{\nu}$ . Solution of the equation then gives a linear relationship in the concentration logarithm with the residence time. The expression for the concentration logarithm at any residence time can be written as:

$$\ln \frac{C_o - C^*}{C_i - C^*} = -k_v t$$
 (4)

where  $C_o$  is the outlet concentration (mg/L),  $C_i$  is the inlet concentration (mg/L).

The determination of the background concentration  $C^*$  is the process related to each factor of the wetland and the interrelationship among them. Therefore, there is not a precise definition and a calculation method for the background concentration  $C^*$ .

Based on the above discussion, we conclude that the main source of the background concentration is the heavy metals ionic on the non-degradable materials, which is mainly the heavy metals ionic existed by physic absorption form on the substrate. In our previous research, the experiments on the wetlands at different operation periods showed that the heavy metals accounted for 0.69%-1.98% (coke system) and 1.07%-3.24% (gravel system) of the heavy metal intercepted by the wetlands, respectively. With the operation time of the wetlands increasing, the heavy metals stripped from the wetland would increase. In other words, the background concentration isn't constant, but changes little with the operation time increasing. If the total amount of the heavy metal intercepted by the wetland can be calculated, the expression for the background concentration can be written:

 $C^* = 0.69\% \sim 1.98\%$ (wt) (for Coke system) (5)

$$C^* = 1.07\% \sim 3.24\%$$
(wt) (for Gravel system) (6)

#### 2. Materials and Methods

#### 2.1. Process Description

The wetlands, located in Tongji University of Shanghai, were constructed in 2007. Two wetlands, shown in Figure 1, are filled with two different substrates (coke and gravel) with a packed bed size of 1930 mm×400 mm× 600 mm (L×W×H). PVC rectangular sink with volume of 0.6 m<sup>3</sup> was used for storing cistern. Structural slope is 1% of height of wetland.



Figure 1. Flow chart of the subsurface flow constructed wetlands.

In order to compare with the treating effect of different substrates, coke with particle diameter of 5-10 mm and gravel with particle diameter of 3-8 mm were packed in the different CWs, respectively. The porosity of coke wetland and gravel wetland were 0.43 and 0.36.

Activated sludge was obtained from secondary sedimentation basin in Shanghai Quyang sewage treatment plant. Because reeds have a much better absorption of heavy metals than other species of plants [10,11], the reeds with height of 1.7 m and density of 60 plant/m<sup>2</sup> are used in the experiment.

Wastewater flowed into constructed wetland by Lange peristaltic pump with a model of BT00-300M, speed of 0-300 r/min and a transport regulation range of 0.07-1140 ml/min. In order to make the inflow well distributed and close to the ideal flow patterns, the water distribution pipes, shown in Figure 2, are alternately permutated. The heavy metal wastewater was lifted into the buffer tank by peristaltic pump, and then flowed into the constructed wetlands through the water distribution pipes. After being treated by the CWs, the heavy metal wastewater flowed out of the system through the sampling pipe and outlet pipe.

After the constructed wetland run for a long time, we collected reeds from inlet, medial position and outlet of constructed wetlands. First, the reeds were cleaned, and cut into seven parts. Secondly, the samples were put into crucible, dried at  $70^{\circ}$ C at baking oven for constant weight, and weighted in turn. Thirdly, the samples were incinerated about 40min, put into muffle furnace to heat for 2 h

at 600°C, treated in the processes of nitric acid hydrolysis, extraction and dilution. Finally, the samples were detected, and the heavy metals contents in reeds were determined by atomic absorption spectrometry [12].

#### 2.2. Experiment Reagents

Heavy mental wastewater for experiment was got by Adding heavy metal salts in the water. Copper sulfate, lead nitrate and zinc sulfate are used as heavy metal pollutants. The experiment reagents and their specifications are listed in Table 1.



Figure 2. Drawing of water distribution system.

reagents	specifications	reagents	specifications
sucrose	eatable	magnesium sulfate	analytically pure
anhydrous sodium carbonate	analytically pure	potassium dihydrogen phosphate	analytically pure
ammonium chloride	chemically pure	potassium chloride	analytically pure
copper sulfate	analytically pure	lead nitrate	chemically pure
zinc sulfate	analytically pure	lead nitrate	analytically pure
zinc oxide	reference reagent	hydrochloric acid	analytically pure

Table 1. Experiment reagents and their specifications.

The reference standards for experiment reagents and their specifications are on the GB7475-87 standards for the reagents.

#### 2.3. Experiment Methods and Instruments

The experiment determination standards were concentration of Cu, Zn, Pb, pH, and water temperature. The preparation of the heavy metals analyses for Cu, Zn and Pb was carried out according to China national standards GB7475-87 designed for heavy metals. The concentration of the heavy metals were detected by atomic absorption spectrophotometer (Agilent). The analyzing methods and instruments for determining water temperature according to State Environmental Protection Administration [13] approved methodology were water and exhausted water monitoring analysis method, and mercurial thermometer. According to China national standards GB6920-86, acidimeter was used to measure pH.

#### 3. Results

#### 3.1. Removal Efficiencies of Pb

Based on results over 4 months (September-December

2007) the removal efficiencies of wetlands treating wastewater containing Pb were calculated. The results are listed in Table 2 and Table 3. It is clearly shown in Table 2 and Table 3 that both coke and gravel systems have remarkable removal efficiencies on treating wastewater containing Pb. It was found that the removal efficiencies of the coke system and the gravel system were within 95-99%. The data of those two systems treating Pb had well agreement with the zero order dynamic model rather than the first order dynamic model. It is suggested that the Pb removal efficiencies were mainly determined by the Pb concentrations, but with little relation to hydraulic resident times.

#### 3.2. Removal Efficiencies of Zn

The data for the events of September-December 2007 are listed in Table 4 and Table 5. According to the Equation (5) and Equation (6), the concentrations of Zn were calculated. The results are shown in Figure 3 and Figure 4. It is evident from the figures that the data follow the linear shape predicted by Equation (4). The  $k_{\nu}$  values, for the coke system and gravel system treating wastewater containing Zn were calculated and the results were 0.2326 h<sup>-1</sup> and 0.1222 h<sup>-1</sup>, respectively.

 Table 2. Inlet concentrations, outlet concentrations and removal efficiencies of the coke system treating the wastewater containing Pb at the different hydraulic loadings.

Hydraulic resident time (h)	12.68	10.72	7.99	5.73	4.76
Inlet concentration (mg/L)	27.44	23.46	19.48	21.87	11.53
Outlet concentration (mg/L)	0.0928	0.0795	0.2651	0.2883	0.5726
Removal efficiency (%)	99.66	99.66	98.64	98.68	95.03

Table 3. Inlet concentrations,	, outlet concentrations	s and removal	efficiencies of	f the gr	ravel system	treating the	wastewater
containing Pb at the different	hydraulic loadings.						

Hydraulic resident time (h)	9.60	7.02	5.77	4.76	6.0
Inlet concentration (mg/L)	49.890	40.370	47.009	47.957	43.152
Outlet concentration (mg/L)	0.234	0.394	0.390	0.596	0.587
Removal efficiency (%)	99.53	99.02	99.17	98.76	98.64

Hydraulic resident time (h)	12.68	10.72	5.73	4.76	4.67
Inlet concentration (mg/L)	48.50	21.264	26.37	17.859	31.477
Outlet concentration (mg/L)	4.276	2.218	6.583	5.553	4.712
Removal efficiency (%)	91.18	89.57	75.03	68.91	85.03

Table 4. Inlet concentrations, outlet concentrations and removal efficiencies of the coke system treating the wastewater containing Zn at the different hydraulic loadings.

Table 5. Inlet concentrations, outlet concentrations and removal efficiencies of the gravel system treating the wa	'astewa-
ter containing Zn at the different hydraulic loadings.	

Hydraulic resident time (h)	9.60	7.02	6.0	5.77	4.76	3.20
Inlet concentration (mg/L)	5.268	7.439	5.622	4.603	5.445	7.218
Outlet concentration (mg/L)	2.024	2.526	2.543	2.478	1.401	2.558
Removal efficiency (%)	61.57	66.04	54.77	46.17	74.26	64.55



Figure 3. First-order model fitting drawing of the coke system treating Zn.

#### 3.3. Removal Efficiencies of Cu

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The data for the event of September-December 2007 are listed in Table 6 and Table 7. According to the Equation (5) and Equation (6), the concentrations of Cu were calculated. The results are shown in Figure 5 and Figure 6.



Figure 4. First-order model fitting drawing of the gravel system treating Zn.

It is evident from the figures that the data follow the linear shape predicted by Equation (4). The  $k_v$  values, for the coke system and gravel system treating wastewater containing Cu were calculated and the results were 0.2017 h<sup>-1</sup> and 0.3739 h<sup>-1</sup>, with coefficient of correlation R<sup>2</sup> 0.8801 and 0.8067, respectively.

Table 6. Inlet concentrations, outlet concentrations and removal efficiencies of the coke system treating the wastewater containing Cu at the different hydraulic loadings.

Hydraulic resident time (h)	12.68	10.72	5.73	4.76	4.67
Inlet concentration (mg/L)	28.519	26.189	23.666	18.036	19.783
Outlet concentration (mg/L)	2.639	3.198	5.413	5.269	6.345
Removal efficiency (%)	90.75	87.79	77.10	70.79	67.93

Table 7. Inlet concentrations, outlet concentrations and removal efficiencies of the gravel system treating the wastewater containing Cu at the different hydraulic loadings.

Hydraulic resident time (h)	9.60	7.02	5.77	4.76	3.34	3.20
Inlet concentration (mg/L)	26.515	27.412	26.515	24.006	26.515	28.327
Outlet concentration (mg/L)	0.0735	2.268	2.577	0.0372	1.830	4.982
Removal efficiency (%)	99.72	91.73	90.28	99.84	93.10	82.40



Figure 5. First-order model fitting drawing of the coke system treating Cu.

Both the coke CWs and gravel CWs had good treatment effect on Pb. The results showed that the treatment efficiencies for Pb didn't fit for first order dynamic model. The removal efficiencies of Pb didn't change with the increasing of hydraulic retention time. The volumetric rate constants ( $k_{\nu}$ ) for the heavy metals (Zn and Cu) under consideration were determined by fitting lines to the observation (Table 8).

#### 3.4. Heavy Metals Contents in Reeds

The heavy metals contents of reeds are given in Figure 7. From the analysis of the three heavy metals, it is found that Cu, Zn and Pb contents in reeds of coke system were 0.1667%, 0.2094% and 0.2781%, respectively, and Cu, Zn and Pb contents in reeds of gravel system were

 
 Table 8. First-order model parameters of different substrates treating different heavy metal.

first order dynamic model	substrate	Heavy metal	$\mathbf{R}^2$	$k_V(\mathbf{h}^{-1})$
$c_{-c}^{*}$	coke	Zn	0.8801	0.2326
$\ln \frac{c_o}{c_o - c^*} = -k_V \times t$	_	Cu Zn	0.7830	0.2017
$c_i - c$	gravel	Cu	0.7149	0.3739



Figure 7. Heavy metals contents in reeds of different CWs based on analysis over all samples.



Figure 6. First-order model fitting drawing of the gravel system treating Cu.

0.1645%, 0.1713% and 0.1477%, respectively. The results showed that the heavy metals contents in reed were very few. It is indicted that the reeds didn't have obvious effect on the process of CWs treating heavy metal.

#### 4. Discussion

The removal efficiencies for Pb are higher than the efficiencies for Zn and Cu. These results well agree with the discovery of Walker and Hurl [14]. The same constructed wetland has different rate constants because of the different heavy metals. The results showed that the coke system treating the Zn and Cu didn't have significant differences in the volumetric rate constant. But the volumetric rate constants of the gravel system treating Cu were higher than those of Zn. The Cu and Zn contents of reeds in gravel system didn't have significant differences. It is indicated that the CWs with gravel had better purification effect on Cu than that on Zn.

In the present study, the effects of the two different substrate systems were also investigated. Xu and Zhou found that different substrates had influence in constructed wetland treating heavy metals [3]. The results agree well with the finding of Xu and Zhou. The  $k_v$  value of the coke system treating Zn is higher than that of the gravel system. The  $k_v$  value of the coke system treating Cu is lower than that of the gravel system.

The results indicated that the first order dynamic model had its limitations, for the reason that it can't accurately describe all the heavy metal behaviors in the constructed wetland.

#### 5. Conclusions

The study has been carried out in two constructed wetlands of different substrates (coke and gravel). The study was aimed to determine volumetric rate constants of two different substrates constructed wetlands and compared the removal ability of the different substrates. The volumetric rate constants of the coke system treating Zn and Cu were calculated as 0.2326h<sup>-1</sup> and 0.2017h<sup>-1</sup>. The volumetric rate constants of the gravel system treating Zn and Cu were calculated as 0.1222h<sup>-1</sup> and 0.3739h<sup>-1</sup>. The volumetric rate constants of the different substrates system treating heavy metal varied. The different substrate may affect the removal ability of the constructed wetland.

This study showed that the first order dynamic model did not fit for all the heavy metals retention. The first order dynamic model could predict the Zn and Cu concentration. However, this model fail to predict Pb concentration. Both the Pb removal efficiencies of the coke system and the gravel system were within 95-99% suggesting that Pb retention had little relation to hydraulic resident times. In addiction, the Zn and Cu removal efficiencies of the coke system and the gravel system were within 54-91%, and 69-99% suggesting that the removal efficiencies for Pb are higher than the efficiencies for Zn and Cu.

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# **Reclamation of the Polymer-Flooding Produced Water**

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#### Abstract

In order to resolve the discharge problem of the polymer-flooding produced water (PFPW) in crude oil extraction, the PFPW was treated by a four-grade and four-segment (four GS) electrodialysis reversal(EDR) set-up. The testing results show that the treated PFPW has two kinds, one is the diluted treated PFPW, the total dissolved solids (TDS) of the diluted treated PFPW is less than the original PFPW, the diluted treated PFPW is feasible for confecting polymer solution; another one is the concentrated treated PFPW, the TDS of the concentrated treated PFPW exceeds the original PFPW, the concentrated treated PFPW is feasible for replacing the PFPW as the injecting water in the water-flooding process for high permeability layer. This treatment technology can not only decrease environment pollution resulted by the PFPW discharge, but also achieve closed-circuit of the water resource during crude oil extraction by using polymer flooding technology.

Keywords: Polymer-Flooding Produced Water, Total Dissolved Solids, Electrodialysis, Treatment

### 1. Introduction

In crude oil extraction, water can be injected into the stratum to drive the crude oil out of the ground, which is often termed as water flooding process or secondary oil extraction. The oil content would decrease after the secondary oil extraction is operated for some time. In order to improve the oil recovery, polymer flooding (injected water containing polymer) and alkaline- surfactant-polymer flooding (injected water containing alkaline, surfactant and polymer) would subsequently be used, which is often called as tertiary oil extraction. Industrial experiences show that polymer flooding can enhance oil recovery by up to 12% and plays a key role in the oil exploitation [1,2]. This technology has been widely used in Daqing oilfield in China in recent years [3–5]. Recent statistics show that oil production by polymer flooding in China reached  $10 \times 10^6$  ton in 2006, and Daqing oilfield has the largest polymer flooding project in the world.

Figure 1 illustrates process of tertiary oil extraction by polymer flooding and treatment of produced water. A large quantity of a polymer (hydrolyzed polyacrylamide, HPAM) is dissolved in water to increase the solution viscosity before water is injected into the stratum through water wells. The HPAM solution with some crude oil is then extracted from the oil wells. The produced liquid becomes produced water (oily wastewater) after dehydration process using three-phase separators. And the produced water becomes polymer- flooding produced water (PFPW) after it is further treated. The PFPW contains polymer, oil, calcium, magnesium, Carbonate and so on.

After the removal of oil, grease, suspended solids, and organic compounds, the PFPW is our investigative content. There are few effects of HPAM on treatment of PFPW by four GS EDR technology and the effects of HPAM has been described in another paper [6]. The high total dissolved solids (TDS) concentration in produced water still poses a challenge in the treatment for beneficial use. It is well known that there are some corresponding relation between the viscosity and the TDS of PFPW. When TDS is a little higher, correspondingly viscosity is a little lower, vice versa [7]. However viscosity is one of the most important parameters to achieve polymer flooding. Simulated experimental results showed when TDS is less than the one of surface water, whether at the aspect of viscidity or shear-resistance ability, the quality of the PFPW can always meet all the conditions for oilfield polymer solution confection. So we

can think removing TDS is the key problem to actualize the PFPW reused. Separation technologies that are currently available for desalting produced water include filtration with bentonite membrane [8], reverse osmosis [9,10–12], and electrodialysis (ED) [6]. Most of the published work on the removal of TDS from oilfield produced water was addressed with the use of reverse osmosis, few scaled-up tests of electrodialysis has been performed for this application [6]. The reduction of TDS in produced water with ED is the focal point of this paper.

In ED, electrolytes are transferred through a system of solutions and ion-exchange membranes by an applied electric potential gradient. An ED stack consists of cation-exchange membranes, which are permeable to positively charged ions but not to negatively charged ones, and anion-exchange membranes, which are permeable to negatively charged ions but not to positively charged ones. In the stack, cation-exchange membranes alternate with anion-exchange membranes to form solution compartments. When an electrical potential is applied between the electrodes at the end of the stack, all cations in the solution circulating through the stack tend to move toward the cathode and all the anions tend to migrate toward the anode. The cations that migrate through cation exchange membranes toward the cathode are rejected by anion-exchange membranes; simultaneously, the anions that pass through anion-exchange membranes toward the anode are rejected by cation- exchange membrane. As a result, ion depletion and concentration are accomplished in alternating solution compartments. The diluate streams from the alternating compartments are combined and distributed back to the

same compartments to continuously remove the ions from the diluate. An analogous process occurs to continuously increase the ions in the concentrate [13].

In order to reduce the risk of caused scaling by concentration polarization and suspended solids adsorbing, this set-up adopts four-grade and four-segment (four GS) electrodialysis reversal (EDR) technology to desalinate the PFPW. Through the test results, the conductivity of the treated PFPW was under 1.3mS/cm and the energy consumption for producing 1m<sup>3</sup> diluted treated PFPW was less than 1kW·h. keeping the flowrate ratio of concentrated and diluted treated PFPW as 1:1, as well as varying the flowrate and voltage, the removal rate under different flowrate was measured. The optimal operating conditions were studied. In optimal conditions, the available uses of the diluted treated PFPW and the concentrated treated PFPW were analyzed.

#### 2. Experiment

The test equipment is shown in Figure 2. This set-up consists of feed water pump, drainage pump, feed water pipes, draining pipes, flowmeters, four GS EDR membrane stack (the active area of a membrane is  $400 \times 1600$  mm<sup>2</sup>. There are 4 segment membrane stacks. Each segment membrane stack consists of 75anion-exchange, 76 cation-exchange membranes and 150spacers which are arrayed alternately), 5pairs of Ti-Ru electrodes, automatic control cabinet, rectifier cabinet, online conductivity meter, 20kW transformer, air compressor, draining tank and pickling tank.



Figure 1. Process of tertiary oil extraction by polymer flooding and treatment of produced water.



Figure 2. Test equipment.

#### 3. Results and Discussion

Firstly, electrical potential difference and feed water were applied in the set-up. Under the condition of adopting four GS electrodialysis reversal technology, keeping the flowrate ratio of concentrated and diluted treated PFPW as 1:1, as well as varying the flowrate and voltage, the removal rate under different flowrate was measured. The results are shown in Figure 3.

Under this operating condition, when the flowrate was  $3m^3/h$ , the minimal removal rate of TDS was 77.4%; the maximal removal rate of TDS was 94.4%. When the flowrate was  $4m^3/h$ , the minimal removal rate of TDS was 90.6%. When the flowrate was  $5m^3/h$ , the minimal removal rate of TDS was 75.8%; the maximal removal rate of TDS was 75.8%; the maximal removal rate of TDS

was 84.3%. According to the test results, it is analyzed that their common operating characteristics are that with the rise of operating voltage, the removal rate of TDS increases, but the treated PFPW conductivity decreases; at the same voltage, with the rise of the flowrate, the removal rate of TDS decreases, the greater the flowrate was, the lower the removal rate of TDS was; at the same removal rate, the greater the flowrate was, the higher the applied voltage was.

Because the set-up pressure can only provide the flowrate of  $11\text{m}^3/\text{h}$ , in order to determine the maximum treating capacity, the flowrate of the concentrated treated PFPW was reduced, the flowrate of the diluted treated PFPW was increased, and the total flowrate was  $11\text{m}^3/\text{h}$ . A testing (the flowrate of the concentrated treated PFPW was  $4\text{m}^3/\text{h}$ , the diluted treated PFPW was  $6\text{m}^3/\text{h}$ , the diluted treated PFPW was  $6\text{m}^3/\text{h}$ , the rinse solution was  $1\text{m}^3/\text{h}$ .) was carried out. The results were shown in Figure 4.When the flowrate of the diluted treated PFPW was  $6\text{m}^3/\text{h}$ , its conductivity can be under 1.3mS/cm by increasing the voltage, but the energy consumption reached 1.4kW·h/m<sup>3</sup>, which exceeds the design standards. So the maximum treating capacity of the diluted treated PFPW was  $5\text{m}^3/\text{h}$ .

The lower the flowrate of concentrated treated PFPW, the higher the concentration ratio. Due to that reason, when the concentration difference is much bigger, the selectivity of membranes would be decreased, the reverse osmosis of TDS be increased, which results in the decrease of current efficiency, and the decrease of TDS removal rate. Under the condition of adopting four GS, when the flowrate of the rinse solution was  $1m^3/h$  and the diluted treated PFPW was  $5m^3/h$ , varying the flowrate of the concentrated treated PFPW, the energy consumption was determined at different ratio of concentrated and diluted treated PFPW.



Figure 3(a). Four GS operation effect under 3m<sup>3</sup>/h flowrate.



Figure 3(b). Four GS operation effect under 4m<sup>3</sup>/h flowrate.

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Figure 3(c). Four GS operation effect under 5m<sup>3</sup>/h flowrate.

As shown in Figure 5, when the flowrate of the diluted treated PFPW was 5m<sup>3</sup>/h, reducing the flowrate of the concentrated treated PFPW, the energy consumption of the same removal rate of TDS were less than 1  $kW \cdot h/m^3$ . But the basic trend is that the lower the flowrate of the concentrated treated PFPW, the higher the energy consumption. When the conductivity achieved 1.3mS/cm, which is the stated value, and the flowrate of the diluted treated PFPW was 5m<sup>3</sup>/h, the energy consumption was the lowest. When the flowrate of the concentrated treated PFPW was 2m<sup>3</sup>/h, the diluted treated PFPW was 5m<sup>3</sup>/h and the energy consumption was 0.89kW·h/m<sup>3</sup>. In order to enhance the production rate and meet the request for energy consumption, the selected flowrate of the concentrated and the diluted treated PFPW was 2m<sup>3</sup>/h and 5m<sup>3</sup>/h respectively.



Figure 5. Relation between conductivity and energy consumption at different flowrate of the concentrated treated PFPW.



Figure 4. Relation between conductivity and energy consumption.

Under the condition of adopting four GS, the optimal operating conditions are: the flowrate of the rinse solution was  $1m^3/h$ , the diluted treated PFPW was  $5m^3/h$ , and the concentrated treated PFPW was  $2m^3/h$ .

In optimal operating conditions, the treated PFPW has two kinds, one is the diluted treated PFPW whose TDS is less than the original PFPW, the diluted treated PFPW is feasible for confecting polymer solution; another one is the concentrated treated PFPW whose TDS exceeds the original PFPW, the concentrated treated PFPW is feasible for replacing the PFPW as the injecting water in the water-flooding process for high permeability layer. The water quality data about the PFPW, the diluted treated PFPW and the concentrated treated PFPW are presented in Table 1.

The pH values of three types of water are different, as shown in Table 1. The pH of the diluted treated PFPW was lower than the original PFPW, but the pH of the concentrated treated PFPW was higher than the original PFPW. This is because after the original PFPW was treated by the ED set-up, the most HCO<sub>3</sub><sup>-</sup> that influencing the pH of the original PFPW was concentrated into the concentrated treated PFPW. The HCO<sub>3</sub><sup>-</sup> of the diluted treated PFPW decreased from 2803 mg/L (in the PFPW) to less than 1000mg/L. So the pH of the diluted treated PFPW was deceased due to the reduction of HCO<sub>3</sub><sup>-</sup>. Finally the pH of the diluted treated PFPW was 7.78, which is alkaline, and it would not lead any corrosion to the preparation and injection equipments and pipelines. Seen from Table 1, the concentrations of some divalent ions such as Ca<sup>2+</sup>, Mg<sup>2+</sup> are little, so they can not cause scaling when the concentrated treated PFPW was used as the injecting water in the water-flooding process for high permeability layer. It fully meets the pH requirement of confecting polymer solution in oilfields. Therefore, the diluted treated PFPW can be used to confect polymer solution. The pH of the concentrated PFPW is a little higher than the original PFPW. The TDS of the concen-

	Original PFPW	Diluted treated PFPW	Concentrated treated PFPW
рН	8.50	7.78	8.80
$K^++Na^+(mg/L)$	1474.5	245.2	2398.8
$\operatorname{Ca}^{2+}(\operatorname{mg/L})$	16.0	8.0	44.1
$Mg^{2+}(mg/L)$	4.9	2.4	2.4
Cl <sup>-</sup> (mg/L)	895.4	97.5	1524.9
$SO_4^{2-}(mg/L)$	96.1	67.3	38.4
$HCO_3^{-}(mg/L)$	2135.7	427.2	3417.1
$CO_3^{2-}(mg/L)$	75.0	0.0	180.1
Polymer (mg/L)	150.3	146.7	151.4
Suspended solids (mg/L)	3.0	2.8	2.9
Oil (mg/L)	2.6	2.7	2.8
TDS (mg/L)	4697.6	847.6	7605.7

Table 1. The characteristics of PFPW being used in the test.

trated treated PFPW was about twice of the PFPW. Because there is no specific requirement for the TDS in the injecting water for water flooding in the high permeability layer, the concentrated PFPW with a little higher pH than the PFPW would not bring any effect on water injection production. Therefore the concentrated treated PFPW is feasible to be used to replace the original PFPW as the flooding water in the high permeability layer.

#### 4. Conclusions

This set-up adopts four-grade and four-segment (four GS) electrodialysis reversal technology to desalinate the PFPW. Under the condition of adopting four-grade and four-segment, keeping the ratio of concentrated and diluted treated PFPW flowrate as 1:1, as well as varying the flowrate and voltage, the removal rate under different flowrate was measured. The optimal operating conditions were studied. In optimal operating conditions, the available uses of the diluted treated PFPW and the concentrated treated PFPW were analyzed. Based on the test results, the optimal operating conditions are as follows: the flowrate of the rinse solution was  $1m^{3}/h$ , the diluted treated PFPW was  $5m^{3}/h$ , and the concentrated treated PFPW was 2m<sup>3</sup>/h. In optimal conditions, the testing results show that the treated PFPW has two kinds, one is the diluted treated PFPW whose TDS is less than the original PFPW, the diluted treated PFPW is feasible for confecting polymer solution; another one is the concentrated treated PFPW whose TDS exceeds the original PFPW, the concentrated treated PFPW is feasible for replacing the original PFPW as the injecting water in the waterflooding process for high permeability layer. This treatment technology can not only decrease environment pollution resulted by the PFPW discharge, but also achieve closed-circuit of the water resource during crude oil extraction by using polymer flooding technology.

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#### Abstract

Adsorption and desorption mechanisms of methylene blue (MB) removal with iron-oxide coated porous ceramics filter (IOCPCF) were investigated in batch and column mode. The results revealed that MB removal mechanisms included physical adsorption and chemical adsorption, of which chemical adsorption by surface ligand complex reaction played a dominant role after infrared spectrum analysis. Recycling agents were selected from dilute nitric acid (pH=3), sodium hydroxide solution (pH=12) and distilled water. Among three agents, dilute metric acid (pH=3) was the best recycling agent. Regeneration rate of IOCPCF arrived at 82.56% at batch adsorption and regeneration was finished in 75min at column adsorption. Adsorption-desorption cycles of IOCPCF after batch and column adsorption were four and three times, respectively. Further, compared with fresh IOCPCF, MB removal rate with these desorbed IOCPCF adsorption only slightly decreased, which suggested that IOCPCF should be used repeatedly.

Keywords: Iron-Oxide Coated Porous Ceramics Filter, Adsorption, Desorption, Methylene Blue, Surface Complex Reaction, Reuse

#### 1. Introduction

Dyestuff removal was primary problem in the printing and dyeing wastewater treatment. At present, the ways, such as adsorption, chemical oxidation, catalytic oxidation, biological method and membrane method, were often used [1,2]. Thereinto, adsorption could eliminate organic compounds which were resistant to degradation by biological method or general oxidation, for example, nitroaromatics and hetero-cyclic compounds, and it took on advantages such as simple operation, less land occupation, good effect and so on. So, adsorption was widely employed in the printing and dyeing wastewater treatment.

There are two shortcomings in the printing and dyeing wastewater treatment by active carbon, which is commonly used absorbent: 1) Higher disposing cost limits its extensive use; 2) Active carbon shows shielding effect on dyestuff removal because its pore diameter is smaller than molecular diameter of dyestuff [3]. So, it is vital that low-cost absorbent should be prepared. For instance, more and more adsorbents from farming byproducts and industrial waste were used in the printing and dyeing wastewater treatment because of their rich resource and lower cost [4,5].

Adsorption includes batch and column adsorption, but column adsorption plays a dominant role in the practical application. In order to reduce treatment cost and improve processing efficiency, the absorbent must be better adsorption and desorption performance. Therefore, batch adsorption, column adsorption and their regeneration for MB removal form aqueous solution were implemented using home-made IOCPCF as a absorbent. Adsorption and desorption mechanisms of MB were emphatically analyzed, which hopes to provide theoretical basis for industrial wasterwater treatment by porous ceramics filter.



### 2. Experiment

#### 2.1. Chemicals

All chemicals and reagents used for experiments and analyses were of analytical grade, such as sodium hydroxide, ferric nitrate, MB. Porous ceramics filter based on red mud was kindly provided by Shandong Aluminium Corporation.

#### 2.2. Methods

According to literature 6, surface modification and related performances test of porous ceramics filter, whose particle size is between 1.0mm and 1.2mm, were made. The MB stock solution was prepared by dissolving accurately weighted MB in distilled water to the concentration of 500mg/L. The experimental solution was obtained by diluting the stock solution in accurate proportions to different initial concentrations.

Batch adsorption experiments were carried out in a constant temperature water bath-vibrator at 150rpm and at an ambient temperature (20-40°C) using 150mL conical flask (having plug) containing 50mL of initial MB concentration (100mg/L) and initial pH (11). The initial pH value of the MB solution was previous adjusted with 0.1N NaOH using a pH meter (PHS-3C, China). The adsorbent (5g) was added to each flask, and then the flasks were sealed up to prevent change of volume of the solution during the experiments. After shaking the flasks for predetermined time intervals, the residual MB solution was sampled and determined. Regeneration rate of IOCPCF was calculated according to as follows: 1) After adsorption equilibrium, average adsorption content  $(q_1)$ of IOCPCF was decided; 2) The used adsorbent (5g) was again added to a flask containing 50mL actified solution (one of dilute nitric acid (pH=3), sodium hydroxide solution (pH=12) and distilled water). Then, the flask was shaked for 300min at 30°C. According to forgoing method, the elution amount  $(q_2)$  was decided as well; 3) The ratio of  $q_2$  and  $q_1$  was the regeneration rate.

Filtration column was composed of organic glass (1.07cm inner diameter and 75cm in height). An external circulating bath allowed carrying out the experiments at the desired temperature. At the bottom of filtration column, quartz sands were laid as supporting layer whose thickness was 2cm. A separatory funnel (125mL) was set at its top as an elevated water tank, and then flow rate of MB solution could be regulated by control of piston opening of separatory funnel and filtration column. The height of IOCPCF, initial concentration, initial pH and temperature in filtration column were 40cm, 50mg/L, 11 and 30°C, respectively. Regeneration in column adsorption adopted to dilute nitric acid as recycling agent and flow rate at regeneration was 4mL/min. The sampling interval was 15min.

The MB solution concentrations in the supernatant were estimated by measuring absorbance at maximum wavelength ( $\lambda$ max=663nm) with a 721-spectrophotometer (Shanghai, China) and computing from the calibration curves.

#### 3. Results and Discussion

#### 3.1. Adsorption and Desorption in Batch Mode

Figure 1 shows adsorption kinetics on MB removal at  $20^{\circ}$ C,  $30^{\circ}$ C and  $40^{\circ}$ C in batch mode. It was obvious that the removal rate reduce of MB was rapid during the initial stages. Then MB uptake capacities increased with time and reached equilibrium values at approximately 300min for three temperatures. At the same time, MB uptake capacities enhanced from 0.56mg/g to 0.85mg/g with temperature increase from  $20^{\circ}$ C to  $40^{\circ}$ C, which suggested that the adsorption was endothermic reaction and higher temperature was propitious to MB removal.



Figure 1. Adsorption kinetic curves at different temperature.



Figure 2. Effect of regenerating agent species on regeneration of IOCPCF.

IOCPCF regeneration after equilibrium at  $30^{\circ}$ C by three recycling agents is illustrated in Figure 2. It was seen from Figure 2 that regeneration rate of dilute nitric acid (pH=3) was the highest (82.56% or so), next to NaOH (39.67%) and last to distilled water (11.25%).

In order to examine effect of IOCPCF regeneration on MB removal, four adsorption-desorption cycles were made (Figure 3) and recycling agent was dilute nitric acid. As it is shown in Figure 3, MB removal rate was 72.06% with fresh IOCPCF, namely regeneration cycle was zero. However, MB removal rate reduced to 60.87% after four regeneration cycles. This was attributed to the following reasons: IOCPCF could not completely regenerated and iron modification coat of IOCPCF surface had wee loss (0.001622%) during adsorption and desorption because of vibration [6], which led to some adsorption sites reduce. But compared with fresh IOCPCF, the decrease was not significant. It can be inferred that IOCPCF may be regenerated with dilute nitric acid and reused.

#### 3.2. Adsorption and Desorption in Column Mode

Figure 4 shows breakthrough curves at different flow rate. The breakthrough time reduced from 66min to 9min with flow rate increase from 2mL/min to 4mL/min. When flow rate was 8mL/min, the column had been breakthrough from the beginning, which represented that the flow rate (8mL/min) was too high for the column adsorption experiment. The reasons were that contact time was more between MB and IOCPCF at low flow rate. The empty bed residence time (EBRT) was 18, 9 and 4.5min at flow rate 2, 4 and 8mL/min, respectively. MB uptake capacity was 0.078mg/g according to Thomas model [7] at flow rate 8mL/min.

Figure 5 and Figure 6 shows desorption and reuse of adsorption column after breakthrough at flow rate 2mL/min. As shown in Figure 5, MB from saturated IOCPCF was desorbed fast at the beginning. The value of  $C_t/C_0$ 



Figure 3. Effect of regeneration cycles on MB removal rate of IOCPCF.



Figure 4. Breakthrough curves for MB adsorption on IOCPCF at different flow rate.

was equal to 40.32%. Next the desorption rate decreased gradually. At last desorption finished after 75min. In Figure 6, MB removal rate had no significant difference between regenerative column and fresh column during the initial and middle operation period, but MB removal decreased prominently at the later operation period. The reasons were ascribed to as the following: a small part of adsorption sites in regenerative column could not regenerate, but regenerative column had enough adsorption sites for MB during the initial and middle operation period. However, inadequate adsorption sites resulted in MB removal rate decrease at the later operation period in regenerative column. Like batch adsorption, compared with fresh IOCPCF, the decrease was not significant. It can be inferred that IOCPCF may be regenerated with dilute nitric acid and reused.

#### 3.3. Adsorption Mechanisms of MB Removal

From batch adsorption study, MB uptake capacities enhanced with temperature increase, which followed the features of chemical adsorption. Moreover, IR (Infrared



Figure 5. Desorption curve for MB adsorption on IOCPCF.



Figure 6. Recycling of regenerative adsorption column.



Figure 7. Infrared spectra of IOCPCF before and after adsorbed MB (MB initial concentration: 100mg/L, Temperature: 30°C).

Spectrum) may used for tracking existed chemical reaction and exploring the reaction mechanism. Figure 7 shows IR curves of IOCPCF before and after batch adsorption.

It could be inferred that chemical bonding between MB and related groups of IOCPCF may take place from Figure 7 based on following facts: 1) After adsorption, the stretching vibration adsorption band of hydroxyl groups at 3441cm<sup>-1</sup> was broadening and offset; 2) After adsorp-

tion, the new stretching vibration adsorption bands at 2800–3000cm<sup>-1</sup> and 1422cm<sup>-1</sup> were attributed to methyl and benzene ring framework from MB; 3) After adsorption, the adsorption bands of Si-O-Si or Fe-O-Si groups at 1000–1200cm<sup>-1</sup> broadened as well.

On the basis of above analyses, chemical adsorption of MB happened by the following two chief ways:

1) Surface ligand complex reaction

Based on surface ligand theory, surface ligand complex models between IOCPCF and water interface were cited as the following [8,9]:

a) The surface protonic ionization reaction

Surface ferric-oxide compounds of IOCPCF existed in aqueous solution in three forms after hydration, i.e.,  $\equiv FeOH_2^+$ ,  $\equiv FeOH$  and  $\equiv FeO^-$ , and then they may mutually transform according to following forms:

$$\equiv FeOH_2^+ \Leftrightarrow \equiv FeOH + H^+ \tag{1}$$

$$\equiv FeOH \iff FeO^- + H^+ \tag{2}$$

b) The adsorption of MB cation

MB existed in aqueous solution in cation ( $[C_{16}H_{18} N_3S]^+$ ) which reacted with the above ferric-oxide compounds by the following forms:

$$= FeOH + \left[C_{16}H_{18}N_3S\right]^+ \iff = FeO\left[C_{16}H_{18}N_3S\right] + H^+$$
(3)

$$2(\equiv FeOH) + \left[C_{16}H_{18}N_3S\right]^+ \Leftrightarrow (\equiv FeO)_2\left[C_{16}H_{18}N_3S\right] + 2H^+$$

$$= FeOH + [C_{16}H_{18}N_3S]^+ + H_2O \iff FeO[C_{16}H_{18}N_3S]OH + 2H^+$$
(5)

Thus, MB was removed by the formed complex.

2) Hydrogen bond forming

Nitrogen atoms from MB have awful attracting electron ability and less atom radius, so they can form hydrogen bond with hydroxyl groups from IOCPCF surface. Figure 8 explained the hydrogen bond forming process.



Figure 8. Hydrogen bond formation between adsorbent and MB.

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Figure 9. FTIR curves of regeneration of IOCPCF after absorbed MB.

In addition, adsorption isotherms (omitted) of MB presented "S" type rather than "L" type and the adsorption activation energy was 16.1445kJ/mol which was slightly higher than 4.184kJ/mol (physical adsorption), which suggested that physical adsorption, including static adsorption and van der waals force adsorption, was one of mechanisms of MB removal.

#### 3.4. Desorption Mechanisms of MB

Many hydrogen ions in acid medium urged the above equations to move towards the left side, so  $[C_{16}H_{18}N_3S]^+$  adsorbed by complex reaction released from IOCPCF surface. Farther,  $\equiv FeOH_2^+$  was chief existing form of iron-oxide compounds in acid medium, so  $[C_{16}H_{18}N_3S]^+$  was desorbed also by static adsorption.

From Figure 9, it was seen that regeneration of IOCPCF was not complete to both batch adsorption and column adsorption. Comparatively speaking, regeneration effect of batch adsorption was better than that of column because the adsorption bands at 2800-3000cm<sup>-1</sup> were no apparent in regeneration IR curve after batch adsorption, but there were these bands, whose intensity decreased in comparison to no regeneration, in regeneration IR curve after column adsorption. At the same time, the adsorption bands at 1422cm<sup>-1</sup> were all apparent in both adsorption regeneration IR curves. The MB may be adsorbed by surface ligand complex reaction, whose regeneration need damage chemical bond. In addition, regeneration time of batch adsorption was longer than that of column time.

#### 4. Conclusions

On the basis of the experimental results of this investigation, the following conclusions could be drawn:

1) IOCPCF was found to be an effective adsorbent for MB removal.

2) Major mechanism of MB adsorption was surface ligand complex reaction between MB and functional groups of IOCPCF surface, and then there were physical adsorption such as static adsorption and van der waals force adsorption also.

3) Regeneration of IOCPCF was not complete to both batch adsorption and column adsorption. Comparatively speaking, regeneration effect of batch adsorption was better than that of column.

4) Reverse reaction of surface ligand complex reaction and homologous charge repulsion were chief mechanisms of MB desorption.

#### 5. Acknowledgements

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# **3D** Water Environment Simulation for North Jiangsu Offshore Sea Based on EFDC

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#### Abstract

The underwater topography in the offshore sea area of north Jiangsu is complicated, including the middle radial sand ridges and northern Haizhou bay underwater shoal. Therefore, it forms special marine dynamic conditions and typical shoal wetland ecosystem. Previous researches of these sea areas were mainly focused on the forms of morphogenesis and the characteristic of conformation of sand ridges. Few studies have done on three dimensional hydrodynamic and water quality simulation. This paper introduced EFDC (Environmental Fluid Dynamics Code) to study the tidal current fields, dilution and diffusion of the sewage outlet near Yangkou Port. Comparison between computation results and the observed data indicates that this model could reasonably simulate hydrodynamic fields. Based on the computed tidal current field, the distributions of COD concentration were simulated. The range of contamination diffusion derived from sewage outlet was very limited, and the influence range of sewage came to the maximum when ebb slacks in neap tide period.

Keywords: EFDC, Water Quality, Radial Sand Ridges, Numerical Simulation

### 1. Introduction

Due to long-term environmental pollution, over-exploitation and other reasons, overall coastal water environment and quality of north Jiangsu have continued to drop. Especially in recent years, with the increase in sea and land-sourced pollution, ecosystem must burden more pressure. The environmental pollution and local eutrophication have become increasingly serious. Three years of ecological monitoring results show that the ecosystem is subhealth in north Jiangsu. Sea and land-sourced pollution and beach reclamation are main factors which have influenced the water quality environment.

Research domain includes the radial sand ridges which are complicated underwater topographies, located in seaboard of Jiangsu Province, which is in the sea area of south continental shelf in the Yellow Sea, from Sheyang Estuary southwardly to Songzhi Port in the north of the Yangtze River, that is, in the area between the delta submerged by water of the abandoned Yellow River and the delta submerged by water of the Yangtze River. Plan sketch of computation domain and observed stations is shown in Figure 1.

Radial sand ridges system is situated in the area between 32°00'N and 33°48'N, with the length of 199.6km, between 120°40'E and 122°10'E, with the width of 140km, which spans more than 20,000km<sup>2</sup> in the southwest Yellow Sea, and is fan-shaped and stretches from Jianggang toward the sea. The depth of sea area varies from 0 to 25m. More than 70 sandbank ridges make up the radial sand ridges system where strong tidal current and great tidal range occurs. Running among the waterways of sandbank ridges, tidal current is the major power to rebuild sandbanks and to erode and sustain the stability of waterways. Study results show that tidal current in part of waterways which are in sandbank ridges obviously has to-and-fro movements, and nearly does not exchange with adjacent waterways across sandbanks [1].

Research domain has a special kind of tidal surrounding. The Pacific tidal wave from southeast and reflective tidal wave from Shandong peninsula in northwest converge nearby Jianggang, where revolving standing wave forms [2]. The area in the north of Jianggang is influenced by revolving tidal wave system, while the area in



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Figure 1. Plan sketch of study domain and observed stations.

the south of Jianggang is influenced by Pacific traveling tidal wave. Not only do two tidal wave systems enlarge the tidal range of shallow sea in the area of radial sand ridges, but also shape the radial tidal current field.

Previous main researches of north Jiangsu offshore sea area were focused on the forms of morphogenesis and the characteristic of conformation of sand ridges. Few studies have done on three dimensional hydrodynamic and water quality simulation. This paper applied EFDC to study the dilution and diffusion characteristics of sewage outlet near Yangkou Port.

#### 2. Hydrodynamics and Water Quality Model

Environmental Fluid Dynamics Code (EFDC) model was selected for this study. It is a public domain, curvilinear-orthogonal horizontal coordinates, stretched vertical (sigma) coordinates, coupled hydrodynamic, waterquality, and sediment transport model developed by Hamrick (1996) [3]. It is maintained by TetraTech Inc. and is currently being supported by the U.S. Environmental Protection Agency. It is very versatile and can be used for 1, 2, or 3-dimensional simulation of rivers, lakes, estuaries, coastal regions and wetlands. The solution technique used is a finite volume-finite difference spatial discretization with a staggered C grid. The Mellor and Yamada (1982) 2-1/2 order turbulence closure model is used [4]. This turbulence closure model relates the vertical turbulent viscosity and diffusivity to the turbulent intensity, turbulent length scale and Richardson number.

The water quality component of EFDC is based on water quality kinetic from the Chesapeake Bay three-

dimensional water quality model [5]. A more detailed description of the water quality model can be found in the report by Park et al. (1995) [6]. The water quality models can be executed simultaneously with the hydrodynamic component of EFDC, or EFDC simulated hydrodynamic transport fields can be saved, allowing the EFDC code to be executed in a water quality only simulation mode. The computational scheme used in the internal water quality models employs a fractional step extension of the same advective and diffusive algorithms used for salinity and temperature, which guarantee positive constituent concentrations. A novel ordering of the reaction sequence in the reactive source and sink fractional step allows the linearized reactions to be solved implicitly, further guaranteeing positive concentrations. The water quality models accept an arbitrary number of point and nonpoint source loadings as well as atmospheric and ground water loadings.

The EFDC model is capable of simulating a diverse range of environmental flow and transport problems, often addressing critical questions related to both the health of human being and the health of natural ecosystems. With many benefits and advantages brought by the EFDC model, it was applied to study the dilution and diffusion characteristics of sewage outlet near Yangkou Port in North Jiangsu.

#### 3. Analysis and Computation

The computation grid and observed station distributions are shown in Figure 1. Computation adopted orthogonal

curvilinear grid which was preferably fit for the natural boundary, and refined around sewage discharge outlet. A total of 2901 effective computational grids were used. Eight vertical sigma layers were currently being used. In order to reflect the contaminant transport and diffusion in natural tidal field better, this paper calculated tidal current field and contamination diffusion field under the continuous 60 tidal periods, at the end of which the concentration field of contamination diffusion was in stable state. The open boundary of the model was presented by tidal wave model in the East China Sea. During the simulation, time step was assumed as 10 seconds, and water elevation was specified as open boundary which was obtained by 11 harmonic components. Because computation domain was larger enough and there was the long distance between sewage outlet and open boundary, we assumed that there was no diffusion in open boundary.

During simulation, time step assumed 10 second, and water elevation was specified as open boundary which obtained by 11 harmonic components of  $M_2$ ,  $S_2$ ,  $N_2$ ,  $K_2$ ,  $K_1$ ,  $O_1$ ,  $P_1$ ,  $Q_1$ ,  $M_4$ ,  $MS_4$  and  $M_6$ . There is a radial sand ridges system in computation domain, which is submerged when tide rises and reveals when tide falls. Thus, in hydrodynamics simulation, drying and wetting switch was applied. When tide falls, beach reveals, and corresponding grid nodes do not participate in computation, while tide rises, beach is submerged, and corresponding grid nodes participate in computation. The criterion of identification is critical depth, and 0.1m assumed as the critical depth. Salinity and temperature assumed common value, the average annual value for salinity and temperature of north Jiangsu offshore sea was 31‰ and 12°C, respectively.

#### 3.1. Analysis and Computation of Hydrodynamics

The observed surface elevation from May 23rd of 2005 to

June  $8^{th}$  and flow velocity and direction during 23rd of 2005 to June  $8^{th}$  which contain spring, medium and neap tide were used to calibrate this model. The tidal elevation was verified at station Z1, Z2, Z3. The tidal current was verified at station 1#, 2#, 3#, 4#, 5#, 6#. The specific distributions are shown in Figure 1. The verification results of three tidal elevations are shown in Figure 2.

There was a good agreement between the numeric solutions and observed data of tidal elevation. There was a small error between observed tidal elevations and the computation values. One reason of which may be that the wave influence was not considered. Another reason may be that the underwater topography of the radial sand ridges has been strenuous variety that is caused by sediment erosion and deposition, and this paper didn't consider about that. Maximum tide range of this measurement in station Z1, Z2, Z3 are respectively 7.3m, 6.2m, 5.6m. The observed date and computed values are shown in Figs.3. Tide range evidently diminishes along shore from north to south. The areas of station Z1, Z2, Z3 belong to classical semidiurnal tide.

Vertical velocity verification plots are shown in Figure 3, whose velocity is positive when flow direction is no less than  $0^{\circ}$  and no larger than  $180^{\circ}$  with north direction otherwise negative. In addition, the direction is measured in degrees clockwise from the north. In all the figures, the points represent the observed data and the continuous lines represent the computed values. There are too many velocity verification plots, for paper's length, here only plots the verification of station 1#, 2#, 3#. It can be seen clearly that there is a good agreement between the numeric solutions and observed data of velocity amplitude and direction. Vertical distribution of the velocity of surface, middle and bottom layer shows that the surface velocity is larger than the bottom velocity, but the velocity direction was almost consistent.



Figure 2. Comparison of observed and computed tidal levels.



Figure 3. Comparison of observed and computed velocity at the surface, middle and bottom layer.

Current velocity fields in spring tide are larger than that in middle and neap tide. There are radial sand ridges in the computation domain, which are submerged when tide rises and reveal when tide falls. This is consistent with results of other researchers. The area of radial sand ridges is a special kind of tidal surrounding. This special underwater topography and tidal surrounding not only enlarge the tidal range of shallow sea in the area of radial sand ridges, but also shape the radial tidal current fields. The results of study show that tidal current in part of waterways which are in sandbank ridges obviously has to-and-fro movement, and revolving movement occurs in other area.

#### 3.2. Analysis and Computation of Water Quality

For contaminant transport computation and analysis, the sewage outlet which lies near Xiaoyangkou, Rudong, Nantong city is chosen, its location is about 32°36'N, 120°56', where the normal daily sewage discharge to the Yellow sea was about 2×10<sup>4</sup>m<sup>3</sup>. The discharge concentration was 100mg/l, thus the source was 23.1g/s. Considering about machinery, power failure leads to the fact that the wastewater is directly discharged into the Yellow Sea, the discharge concentration was 1000mg/l. So the source was 231g/s. The specific location is shown in Figure 1. According to the requirement of environmental protection regulations, mixing area formed in water area of sewage outlet should not affect the function of neighboring water area, therefore, prediction of outlet contamination concentration and analysis of influence to the accepting water are necessary.

Chemical oxygen demand (COD) was selected as the

reference computation factor of contamination transport. In the process of calibrating model parameters, considering about the realistic condition in Jiangsu coastal area, turbulent diffusion theory and correction of measured data were applied to calibrate the horizontal diffusive coefficient; the degradation coefficient is related to water property, contamination concentration and water temperature etc. After consulting the related handbook at home and abroad, we took the value of degradation coefficient *K* is which adopted in contaminant transport model commonly as a constant. Debugging the degradation coefficient from 0.02-0.08/d, by computation K finally was selected to 0.03/d [7]. The two dimensional hydrodynamic and water quality simulation of the North Jiangsu near Xiaoyangkou was studied by Luo [7,8].

This paper studied the three dimensional distribution of the water quality near Xiaoyangkou. In the process of computation, the concentration of COD which has been treated by sewage plant provided by the draining contamination was 100mg/L. After hydrodynamics computation, we repeated the contamination computation until obtaining about one month stable concentration distributions and then analyzed the results to obtain the increase value of the concentration.



Figure 4. COD surface layer contour distribution of neap tide. Only region near the sewage outlet is shown here for clarity.

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The vertical distribution of the COD concentration contours was similar at the surface, middle and bottom layers. So here only shows the contamination concentration distributions in neap tide period at the surface layer during the entire simulating process in Figure 4. The values of COD contour from inner to outer are respectively 10, 1, 0.1, 0.07, 0.03mg/L. Only a region near the sewage outlet is shown here for clarity and the dotted lines frame of this region is just shown in Figure 1. In one neap tide period, during flood, current velocity is large, while diffusion range of contamination is small. Influenced by tidal current, contamination diffusion trends along the northwest direction, which agrees with the velocity direction and underwater topography; when flood slacks, contamination traces along the velocity direction and waterway upward to the farthest, then influenced by ebb current, contamination starts to run along the southeast direction, and nearshore current still runs shoreward, but sea water in offshore area has begun to run offshore direction; during ebb, in simulation area, the directions of current velocity are all along the offshore direction, contamination from sewage outlet along the northwest direction begins to diffuse along the ebb current, and velocity gradually diminishes; when ebb slacks, revolving current begins to appear, at the same time the diffusion of contamination which follows the tidal current reaches to the longest distance.

During spring and middle tide period, when flood peaks, flood slacks, ebb peaks and ebb slacks, structure properties of tidal current and distribution shape of contamination diffusion are similar to those in neap tide period. And direction of contaminant diffusion is strongly influenced by the velocity direction and underwater topography. Because the sewage outlet is adjacent to the waterway near Xiaoyanggang, the sewages have been wide-range dilution in the waterway before diffusing into the open sea. So the increasing value of contamination concentration introduced by sewage outlet is very limited. As a whole, because of small current velocity and weak tide force in neap tide period, during all simulation process, the variation of diffusion and transport range is smaller than that in spring tide period. Due to weak tidal current and dilution capability, diffusion and transport range of contamination is much larger than that in spring and middle tide period. Here only the COD contour distributions of neap tide are shown in Figure 4. During spring and middle tide period, plan structure of tidal current fields and distribution shapes of contamination diffusion are similar to those in neap tide period. This paper doesn't list these all. During the whole simulation process, differences of these are that velocity in neap tide period is less than that in spring and middle tide period, and variable range of contaminant diffusion and transport in neap tide period is less than that in spring and middle tide period. But supplied water by tide force in neap tide period is also little and obvious, so range of contaminant

diffusion and transport in neap tide period is strongly larger than that in spring and middle tide period.

Enveloping plane of concentration increment is shown in Table 1. The largest enveloping plane of COD contour appears in the middle layer, where the sewage outlet is disposed. And the smallest enveloping plane of COD contour appears in the surface layer. When the concentration increment equals to 10mg/L, the area of surface enveloping plane equals to 0 in the surface layer. When the concentration increment equals to 15mg/L, the area of enveloping plane also equals to 0 in the middle and bottom layer. It shows that the concentration increment of COD caused by sewage disposal is less than 15mg/L in the whole sea area. Based on water quality standards, the sea water is clear where the concentration of COD to be equal or lesser than 4mg /L. In the calculation domain, the area of concentration in the surface, middle and bottom layer more than 4mg/L is 0.96km<sup>2</sup>, 1.29km<sup>2</sup> and 1.02km<sup>2</sup> respectively.

Sewage discharged from the outlet into the sea transport with the direction of flow. The plume of sewage has larger swing with the flow, and the shape of the plume is similar in the surface, middle and bottom layer. Comparison with concentration distribution of different layers, the area of middle layer where the sewage discharged is more than that of the surface and bottom layer.

From the vertical direction, as a result of sewage outlet disposed at the middle layer, the high concentration of COD district appears the vicinity of outlet. With the amount of sewage constantly blending with the surrounding seawater, the concentration of sewage reduces because of the process of rise and fall flow continuously. The high concentration appears in the middle layer, in which sewage discharge outlet disposed.

#### 4. Assessment and Measure

Protection of the marine environment of Jiangsu Province officially began from December 1, 2007, which marked that there are laws for marine ecological and environmental protection of north Jiangsu offshore sea and it also strengthen the protection of the marine environment, and preserve the marine health. These are driving the development of marine industry and beach exploitation.

There are a lot of remarkable progresses in the forms of morphogenesis and the characteristic of conformation of sand ridges, which are availing the research of ecosystem health and its risk assessment. But it is still impossible to predict with confidence the ecosystem health with any degree of certainty in north Jiangsu offshore sea. So it is significant to discuss the material transport near the south Yellow Sea and its influences on marine ecosystem health. Few studies have done on ecosystem health and risk assessment. Due to long-term environmental pollution and

Table 1. The largest enveloping plane of COD contour for slack ebb of neap tide (km<sup>2</sup>).

Layers	Time	3mg/L	4mg/L	5mg/L	7mg/L	10mg/L	15mg/L
Surface	Clash abb	2.20	0.86	0.60	0.16	0.00	0.00
Middle	nean tide	3.36	1.29	0.95	0.64	0.21	0.00
Bottom	neap tide	2.91	1.02	0.80	0.55	0.12	0.00

over-exploitation and other reasons, overall coastal water environmental quality of north Jiangsu has continued to drop. Especially in recent years, with many large projects such as LNG, nuclear power project and Chemical Park project have been implemented, sea and land-sourced pollution increasing, environment ecosystem must burden more pressure. The serious environment pollution and local eutrophication have become increasingly prominent. Assessment of ecosystem health is urgent in north Jiangsu offshore sea.

Some characteristics of hydrodynamics and water quality have been researched which only considered simple physical quantity of two-dimensional space related with time under the mild-slope underwater topography in north Jiangsu shoal [9–12]. Further studies would be converged on the influence of contaminant, nutrient substance to the ecosystem components, the various functions of the health affected by water, optimization study of Jiangsu coastal wetland protection, beach exploitation, distribution of environment pressure and decision-making response. The reason of water quality deterioration and its countermeasures is the ultimate goal.

#### 5. Conclusions

This paper examines the special hydrodynamics characteristics in radial sand ridges area of the Yellow Sea. EFDC was introduced to study the 3D tidal current fields. dilution and diffusion of the sewage outlet near Yangkou Port. The results of computation show that EFDC could perfectly simulate hydrodynamics characteristics and contaminant transport process when dealing with the coastal water pollution problem. Strong tidal current and great tidal range occur in the computation domain, and the results of study show that tidal current in part of waterways which are in sandbank ridges obviously has toand-fro movement, revolving movement occurs in other area, and nearly does not exchange with adjacent waterways across sandbanks. In the computation process of contamination transport, this paper calculates tidal current field and contamination diffusion field under the condition of containing spring tide, medium tide and neap tide in the continuous 72 tidal periods at the end of

which the concentration field of contamination diffusion is in stable state. The magnitude and direction of current velocity play an important role in diffusion and transport of contamination, and the influence range of sewage comes to the maximum when ebb slacks in neap tide period, but all the final influences are very limited. Moreover, assessment system on ecosystem health would be established in north Jiangsu offshore sea.

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# Experimental Study on the Removal of Arsenic in Waste Water from Semiconductor Manufacturing

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#### Abstract

An effective and economic process for removing arsenic in waste water which is acuminating in the process of etching, cutting and washing in semiconductor industry has been developed in this paper. The proposed technique of arsenic removal is as follows: first pretreatment step is to oxidize arsenite to arsenate by potassium permanganate, second key step is precipitation based on arsenic compound solubility with ferric sulfate and slaked lime under pH adjustment, and the last complementary step is followed by the adsorption of the bentonite with enhanced by activated carbon and organic adsorbent. Experimental results show that under the optimal condition the removal efficiency of arsenic in the waste water is better than 99.99%, or the concentration of arsenic is from its original 100mg/l reduced to less than 10µg/l accordingly.

Keywords: Arsenic, Precipitation, Adsorption, Waste Water, Semiconductor Manufacturing

### 1. Introduction

With the fast increasing requirements of the society and economy, the semiconductor industry is being under strong development. A major environment problem resulted by the compound semiconductor manufacturing is its waste water, which most commonly consist of elements such as arsenic, gallium, indium and phosphorous. These elements dissolve in water in the process of cutting, etching, grinding and lead risk to ecological system [1].

The main purpose of this study is to look for an effective process to reduce arsenic in waste water to level acceptable for water reuse or discharge. After comparing various techniques [2–4], i.e., precipitation, adsorption, ion exchange, reverse osmosis, distillation, evaporation, and electrolysis respectively, a combinative process of precipitation and adsorption has been chosen for its economics and convenience.

### 2. Materials and Methods

#### 2.1. Materials

The waste water samples are collected at a local com-

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pound semiconductor factory in September 2006. Several original major contents are: As of 100 mg/l, pH of 6, and a little of Ga (20mg/l) and In (5mg/l).

Arsenic and other heavy metals in water samples are analyzed by the atomic adsorption spectrometer (AA-70, HP, U. S.). The pH is detected by the pH instrument (PHS-25, Shanghai).

The bentonite is H-type come from Weifang, Shandong. The activated carbon is STR-type come from Shijiazhuang, Hebei. The organic adsorbent is unique made in this study which mainly consisted of vegetable protein. And all of the chemical reagents are of chemical analysis grade.

#### 2.2. Methods

The procedure design for removal of arsenic in waste water is shown in Figure 1.

Because the removal efficiency of arsenate is 30% higher than that of arsenite, KMnO<sub>4</sub> has been selected to oxidize As(III) to As(V) at the beginning which guaranties As(V) is dominant in solution in the continues steps [2,3].

Slaked lime  $(Ca(OH)_2)$  have been applied in pH adjustment and precipitation cooperated with ferric sulfate





Figure 1. Treatment procedure design.

 $(Fe_2(SO_4)_3)$ , because of the high efficiency of the removal of arsenic based on the low solubility of  $Ca_3(AsO_4)_2.3H_2O$  (solubility of 0.013),  $Ca_3(AsO_4)_2.Ca(OH)_2$  (solubility of 0.0023-0.0048), and FeAsO<sub>4</sub>. 2H<sub>2</sub>O (insoluble) [4].

Bentonite has been considered to complement removal of arsenic, which enhanced by activated carbon and organic adsorbent [2,5,6]. Bentonite can reach its absorbing equilibrium quickly with good saturated adsorption amount, and the most important is that it is cost-efficient and easy to obtain. Activated carbon is a classical kind of adsorbent with better saturated adsorption amount, and it is used in a broad way presently. The unique organic absorbent is more effective in the removal of arsenic, and it is easy to produce but a little expensive compared to the two adsorbents above mentioned.



Figure 2. As removal efficiency under different pH.

#### **3.** Results and Discussion

# 3.1. The Removal Efficiency of Ca(OH)<sub>2</sub> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>

After pre-treatment of oxidation, a batch experiment has been taken on the composition of  $Ca(OH)_2$  and  $Fe_2(SO_4)_3$ . The results are shown in Table 1.

From the results (Figure 2) it indicates that pH is a controlled element in this step. If the Ca(OH)<sub>2</sub> is over added the excessive OH<sup>-</sup> can replace  $AsO_4^{3-}$  and make  $AsO_4^{3-}$  dissolve out from the sludge and adsorbent. From the experiment it shows the suitable composition is 0.2g of Ca(OH)<sub>2</sub> and 1ml of Fe<sub>2</sub>(SO<sub>4</sub>) (30%) for 100ml of waste water as well as keeping the pH at neutrality.

Table 1. The batch test of Ca(OH)<sub>2</sub> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.

Original As (mg/l)	Ca(OH) <sub>2</sub> (g/100ml)	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (30%) (ml/100ml)	Remaining As (µg/l)
100	0.025	0.125	154.3
100	0.05	0.25	119.4
100	0.075	0.375	90.2
100	0.1	0.5	56.6
100	0.125	0.625	37.8
100	0.15	0.75	24.3
100	0.175	0.875	15.9
100	0.2	1.0	13.7
100	0.225	1.125	13.8

The arsenic in waste water can be reduced from 100 mg/l to  $13.7 \mu \text{g/l}$  under the optimal precipitation condition, which is quite close to the final requirement.

#### 3.2. The Removal Capacity of Bentonite

A batch experiment has been taken to test the adsorption capacity of bentonite. Twelve samples of 100ml solution which contain arsenic from 5 mg/l to 60 mg/l are added by 1g of bentonite separately. After stirring for 60 minutes under room temperature, the remaining arsenic in water of each sample is detected. The results are shown in Table 2 and Figure 3.

Based on Figure 3 it can be summarized that the saturated arsenic adsorption amount of bentonite is about 5.1mg/g.

Based on the same method, the saturated arsenic adsorption amount of activated carbon (18.3mg/g) and organic adsorbent (21.2mg/g) are also obtained.

# **3.3.** The Optimal Condition for Removal of Arsenic

To find the optimal condition for removal of arsenic in waste water, a batch experiment has been taken on the proportions of chemicals and adsorbents added. Suppose 1 unit of Ca(OH)<sub>2</sub> is represented by 0.10g, 1 unit of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (30%) is represented by 0.50ml, 1 unit of bentonite is represented by 0.175g, 1 unit of activated carbon

Table 2. The batch test of bentonite.

Original As (mg/l)	Remain As (µg/l)	Original As (mg/l)	Remaining As (µg/l)
5	4.7	35	30.5
10	8.8	40	35.1
15	12.9	45	40.02
20	17.1	50	44.97
25	21.4	55	49.9

60

54.89

25.9



Figure 3. The adsorption equilibrium curve of bentonite.

30

is represented by 0.100g, and 1unit of organic adsorbent is represented by 0.025g. The results are shown in Table 3.

It can be concluded that fourteen composition (No.2, 3, 5, 6, 8, 9, 12, 13, 14, 15, 18, 19, 20, and 21) can meet the requirement of arsenic in treated water should be reduced to less than 10  $\mu$ g/l. After consideration both of the economic and technique factors, No.2 is chosen to be the optimal composition for our procedure.

In addition, the process is also efficient to remove gallium and indium in the waste water. After treated the concentrations of gallium and indium are from original 20 mg/l and 5 mg/l respectively reduced to lower than the detecting limit of AA analysis.

### 4. Conclusions

For removing arsenic from waste water which is acuminating in the process of etching, cutting and washing in semiconductor manufacturing, a proposed technique is designed based on technique and economic efficiency. The procedure includes: first pretreatment step is to oxidize arsenite to arsenate by potassium permanganate, second key step is precipitation based on arsenic compound solubility with ferric sulfate and slaked lime under pH adjustment, and the last complementary step is followed by the adsorption of bentonite with enhanced by activated carbon and organic adsorbent.

Table 3. The batch test of removal of arsenic.

Number	Ca(OH) <sub>2</sub>	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	Bentonite	Activated	Organic adsorbent	Remaining As
i tuinooi	(unit)	(unit)	(unit)	(unit)	(unit)	(µg/l)
1	1	1	1	1	1	30.8
2	2	2	1	1	1	9.8
3	3	3	1	1	1	6.2
4	1	1	2	2	2	28.7
5	2	2	2	2	2	9.2
6	3	3	2	2	2	5.8
7	1	1	3	3	3	24.2
8	2	2	3	3	3	8.9
9	3	3	3	3	3	4.6
10	1	1	2	1	1	29.0
11	1	1	3	1	1	24.3
12	2	2	1	2	2	9.3
13	2	2	3	2	2	9.0
14	3	3	1	3	3	5.0
15	3	3	2	3	3	4.8
16	1	1	1	2	2	29.3
17	1	1	1	3	3	26.5
18	2	2	2	1	1	9.6
19	2	2	2	3	3	8.9
20	3	3	3	1	1	5.5
21	3	3	3	2	2	5.3

The optimal composition of reagents for removal of arsenic from 100 mg/l to 10  $\mu$ g/l in 100ml solution can be concluded as 0.2g of Ca(OH)<sub>2</sub>, 0.1ml of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (30%), 0.175g of bentonite, 0.1g of activated carbon, and 0.025g of organic adsorbent.

#### 5. Acknowledgement

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# **Evaluating Economic Benefits of Water Diversion Project** for Environment Improvement: A Case Study

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#### Abstract

The research in this paper was based on the project of water diversion from the Yangtze River to the Taihu Lake which significantly improves water environment of the lake and brings obvious economic benefits for surrounding areas. An analytical framework is developed on evaluating benefits of water supply to Huzhou city from project of water diversion from Yangtze River to Taihu Lake, including: (1) the value-added of water supply on the project are divided into four parts according to the characteristics of Hangzhou-Jiax-ing-Huzhou Plain area. (2) The utilization ratio of water diversion is defined based on the features of water resources. (3) The water supply effects on industries and residents' living are explored using partition coefficient method in Huzhou city. Grey relation technique is used to examine the relationship between water use and industrial development in Huzhou, which aims to clarify the rationality of partition coefficient method. The results indicate that benefit of water diversion from Yangtze River to Taihu Lake to tertiary industry of Huzhou city is the highest, while that of industry is the lowest.

Keywords: Water Environment, Water Diversion, Economic Benefit, Grey Correlation

### 1. Introduction

With rapid economic development and great population increase, contradictions among population, resources, environment and development have become a serious challenge. There are extensive reports on this problem based on developed countries such as American, Britain, Holand and Australia. Gardiner advocated the integrated management of river basin aiming to realize river basin's sustainable development [1,2]. National Rivers Authority (NRA) (1995) in Britain published Thames Basin Agenda 21 and Sustainable Development Strategy [3]. The United States Environment Protection Agency (EPA) has addressed importance to governing river basin since 1990.

Since China's reform and opening policy in 1978, Taihu Lake Basin area has changed rapidly. According to the statistics supplied by Taihu Lake Basin Authority, Ministry of water Resources, P. R. China, in 2005, the area created GDP of 13% with its population of 3.2% and area of less than 0.4% in China; and in 2006, it created GDP of 11.1% with its population of 2.8% and area of less than 0.4% in China. However, poor water conditions have been a factor restricting socio-economic development and causing environmental deterioration. Traditional water supply cannot help to provide more water to meet growing demands [4]. Water is often imported through inter-basin water transfers across national, regional and local boundaries to meet increasing off-stream demands in agriculture, industry, hydropower, and household sectors for economic and social development [5]. The project of water diversion from Yangtze River to Taihu Lake, to some extent, covers the shortage of water.

Diverting Yangtze River water into Taihu Lake is by the Wang Yu River project to introduce water from Yangtze River into Taihu Lake and its ambient plain river area, then by the Taipu River project to supply water for downstream area (e.g., Hangzhou-Jiaxing-Huzhou Plain area) (see Figure 1). It officially started in 2002. By the end of 2006, it has transferred 7.42 billion m<sup>3</sup> water from Yangtze River into Taihu Lake Basin, of which 3.24 billion m<sup>3</sup> into Taihu Lake; at the same time it has supplied 9.02 billion m<sup>3</sup> for downstream area by way of Taipu brake, of which nearly half of water for Hangzhou-Jiaxing-Huzhou area [6].





Figure 1. Sketch map of water diversion from Yangtze River to Taihu Lake.

Huzhou city, a city of Zhejiang province and near south of Taihu Lake, is located in the mid-upriver of Taihu basin. Because of its especial geographic position, Huzhou city is always one of the important cities which greatly benefit from the project of water diversion from Yangtze River to Taihu Lake. In the area, water from Taihu Lake is introduced by using two channels. One is that water from Taihu Lake supplies water for basin lower reaches by way of Taipu River. While water from Taipu River directly enters Hangzhou-Jiaxing-Huzhou Plain area by way of Jing-Hang Grand Canal, You Pond, Da Zheng Pond and Wu Zi Pond. The other is that water from Taihu Lake supplies water for east parts of Hangzhou-Jiaxing-Huzhou Plain area by way of river diversion brakes of East Tiao Xi and Lou Harbor entrances of Taihu Lake.

Based on the practical measure and analysis for years by Taihu Lake Basin Authority, Ministry of water Resources, P. R. China, the results show that in Hangzhou-Jiaxing-Huzhou Plain area the range of influence from water flow are mainly east and west plains of Hangzhou-Jiaxing-Huzhou area with the area of about 3 thousand  $m^2$ , of which Huzhou city is the core beneficial area.

The paper aims in providing an analytical framework for evaluating benefits of water diversion projects.

#### 2. Model Development

In order to analyze the benefits of supply water to the intake area, the method of partition coefficient was employed. That is, the benefits of supply water to the intake area can be computed in creating value-added process according to contribution rate of water to primary industry, industry (included in secondary industry), tertiary industry and residential living.

The benefits of supply water for primary industry, industry, tertiary industry and residential living can be calculated as (1):

$$B_s = V_s \cdot (f_s \cdot q_s \cdot k_s) \tag{1}$$

where s represents the economic sector of interest (e.g., primary industry), B benefit of supply water, V benefit of each cubic water, f partition coefficient, q value-added of water supply and k utilization ratio of water diversion.

Individually, for primary industry, industry, tertiary industry, V can be calculated as (2):

$$V = I/W \tag{2}$$

However, for residential living, V has the form of (3):

$$V = r \cdot e / p \tag{3}$$

In (2) and (3), all the variables are explained as follows.

- I -value-added of each industry
- W –total volume of water use
- r –disposable income of residents
- e-Engel's coefficient
- p –per capita water consumption of every year

Adopting the method of partition coefficient to calculate economic benefits of water supply is one of the methods according to the calculation norm of water resources economics. The method can show the correlation among benefits, inputs and outputs. It has been proved suitable in theory and convenient in practice. The key to use the method is how to define the partition coefficient of benefits of water supply. When partition coefficient is appropriately chosen, the benefits of water supply can be concordant with practical results.

#### 3. Description of Variables

In order to calculate the benefits of water supply B on the project of water diversion from Yangtze River to Taihu Lake, the eight variables, that is, value-added of water supply q, value-added of each industry I, total volume of water use W, partition coefficient f, disposable income of residents r, Engel's coefficient e, per capita water consumption of every year p and utilization ratio of water diversion k, must be given.

#### 3.1. Value-Added of Water Supply

In Hangzhou-Jiaxing-Huzhou Plain area, there are multiple rivers and complex river nets with cross-piercing at the bottom as a big container. The water by diversion from Yangtze River to Taihu Lake can freely flow in the area. Thus allocating the value-added of water supply according to water use ratio can reflect the practical water utilization.

The lines of water diversion in the project of water diversion from Yangtze River to Taihu Lake are mainly two: one is supplying water to Hangzhou-Jiaxing-Huzhou Plain area by passing through the Lou harbors of the circle Taihu Lake; another is by passing through the Taipu River. The value-added of water supply are showed in Table 1. By the end of 2005, the total value-added of water supply to Hangzhou-Jiaxing-Huzhou Plain area has been up to 3.926 billion m<sup>3</sup> by the project.

Based on analyzing the water utilization of Hangzhou-Jiaxing-Huzhou Plain area in 2000, the value-added of water supply to every industry and residential living of Huzhou on the project of water diversion from Yangtze River to Taihu Lake were calculated respectively, as listed in Table 2.

Table 1. Value-added volumes of water supply to Hangzhou-Jiaxing-Huzhou plain area on project of water diversion from Yangtze river to Taihu Lake, 2002–2005 Unit: 10<sup>8</sup> m<sup>3</sup>.

Year	Taipu River	Circle Taihu Lake	Total Value-added of Water Supply
2002	2.65	1.06	3.71
2003	6.5	5.90	12.40
2004	2.66	6.61	9.27
2005	4.06	9.82	13.88
Total	15.87	23.39	39.26

Source: Taihu Lake Basin Authority, Ministry of Water Resources, P. R. China.

From Table 2, we can see that the value-added volume of water supply to Huzhou city on the project is steadily increasing. However, in 2003 the value-added of water supply added to 0.131 hundred million m<sup>3</sup> from the value-added of 0.039 hundred million m<sup>3</sup> in 2002 because the year of 2003 is especially on shortage of water. Thus the water height in Huzhou city in 2003 is above the normal water level so as to keep the water quality stable and alleviate water demand in Huzhou city.

#### 3.2. Utilization Ratio of Water Diversion

The total volume of value-added of water supply by the project of water diversion from Yangtze River to Taihu Lake is not possible to be completely used, of which they are discharged without being used. Thus when the direct economic benefits of water diversion are calculated, the parts of water transmission losses should not be computed. In the paper, the utilization ration of water diversion k is defined as (4):

$$k = q_0 / q \tag{4}$$

where  $q_0$  represents the practical use volume of water diversion and q describes the total volume of water diversion. The value of k is decided by the shortage degree and the use capability of water resources in the researched area. According to the total planning of water resources protection and use capability in Zhejiang province, the utilization ration of water diversion is approximately 0.6 in recent years. Thus the utilization ratio of water diversion in Huzhou city is chosen as 0.6.

#### 3.3. Partition Coefficient

The option of the partition coefficient of benefits of water supply is quite important. The benefits of water supply are not concordant with practical results until the partition coefficient is appropriately chosen.

Table 2. Value-added volumes of water supply to threeindustries and residential living of Huzhou city on projectof water diversion from Yangtze River to Taihu Lake,2002-2005Unit: 10<sup>8</sup> m<sup>3</sup>.

Year	Total Value-add ed of Water Supply	Value-adde d of Water Supply to Primary Industry	Value-adde d of Water Supply to Industry	Value-adde d of Water Supply to Tertiary Industry	Value-added of Water Supply to Residential Living
2002	0.362	0.176	0.072	0.014	0.039
2003	1.210	0.588	0.240	0.046	0.131
2004	0.905	0.439	0.180	0.034	0.098
2005	1.355	0.658	0.269	0.051	0.147

1) Partition coefficient of primary industry

Generally, the increasing of production of farm crop results from the synthetical effects of water, fertilizer, seed, soil improvement and technical measures in primary industry (e.g. prevention from disease and insect pest). Thus, allocating the total value-added of production should be scientifically transacted. According to the computation results of benefits of irrigation for many years in Jiangsu, Zhejiang and Shanghai, the average partition coefficients of primary industry in Taihu Lake are individually shown as follows: it is 0.4 in level water year, 0.53 in low water year or slightly low water year. Thus, according to the situation of rain water in Huzhou city in 2002–2005, we can define the average partition coefficients of primary industry (Table 3).

2) Partition coefficient of industry

By the use of the data in Huzhou Statistical Yearbook (1989–2005) [7], an industrial production function can be showed as (5). The equation can be gained by the regression analysis with total production of industry Y as dependent variable, and fixed assets K, populations of labour force L and total volume of water use of industry W as independent variables.

$$Y = 0.997 K^{0.493} L^{0.534} W^{0.242}$$
(5)

In (5), it indicates that the contribution coefficient of water to industry is about 0.2. That is to say that the total production will increase by 0.2% with the increase of water use of 1%. In recent years, the average value-added rate of industry is near 0.25 in Huzhou city. It shows that the total production of industry will increase by 0.05% with the increase of water use of 1% in Huzhou city. Thus, the partition coefficient of industry in Huzhou city is about 0.05.

3) Other partition coefficient

The contribution rate of water to restore labour force is defined as the partition coefficient of tertiary industry. The value is 0.3 according to Chen [8]. The partition coefficient of residential living is calculated by the contribution rate of all kinds of the living materials to restore labour force. According the viewpoint of the Chen [8], the value is thought as 0.3 in this paper.

#### 3.4. Other Variables

The value-added of each industry I and disposable income of residents r can be attained from Huzhou

Table 3. Average partition coefficients of primary industry in 2002–2005.

Year	2002	2003	2004	2005
Rain Water	Lever water	Low water	Slightly low water	Slightly low water
Average Parti- tion Coefficient	0.4	0.53	0.53	0.53

Statistical Yearbook (2002–2005) [7,9–11]. Total volume of water use W can be obtained from Huzhou Water Resources Bulletin. Engel's coefficient e can be calculated by (5). Per capita water consumption of every year p can be demonstrated by (6).

$$e = e_1 / e_2 \tag{6}$$

$$p = W / Pop \tag{7}$$

where  $e_1$  describes the food expenditure,  $e_2$  shows the total expenditure and *Pop* defines the population in cities and towns. The value of the three variables can be obtained from Huzhou Statistical Years (2002–2005) [7, 9–11].

#### 4. Results

Using (1) and (2), the economic benefits of water supply to the three industries of Huzhou city on the project of water diversion from Yangtze River to Taihu Lake were calculated in the years of 2002–2005, as listed in Table 4.

By (1) and (3), the economic benefits of water supply to the resident living of Huzhou city on the project of water diversion from Yangtze River to Taihu Lake were calculated in the years of 2002–2005, as listed in Table 5.

In Table 4 and Table 5, it indicates that in the years of 2002–2005, economic benefits of water supply for primary industry, industry (included in secondary industry), tertiary industry and the residential living of Huzhou city on the project of water diversion from Yangtze River to Taihu Lake are respectively 1.726 hundred million Yuan, 1.309 hundred million Yuan, 12 hundred million Yuan and 0.415 hundred million Yuan. Among them, economic benefit of water supply for tertiary industry is the highest. And the next is primary industry.

#### 5. Evaluating of Economic Benefits of Water Diversion

Although using the method of partition coefficient to calculate economic benefits of water supply is useful, there are some limitations. For example, more investment in the project of water supply, more economic benefits which is unreasonable in practice. Thus, in order to validate the rationality of adopting the method applied in the Huzhou area, the grey relation analysis method is chosen.

Compared with traditional statistical methods which require more data and time, the grey relation analysis (GRA) only needs minimal data to get reasonable and good results. The technique of grey relation analysis has been applied in many fields. For example, Morita *et al.* [12] applied GRA to examine the annual load demand of the power system in Japan, and drew a conclusion that the grey system for the long-term load forecasting problem

Table 4. Economic benefits of water supply to three indus-tries of Huzhou city on project of water diversion fromYangtze River to Taihu Lake, 2002–2005Unit: 10<sup>8</sup> Yuan<sup>3</sup>.

Year	2002	2003	2004	2005	Total
Primary Industry	0.100	0.492	0.493	0.641	1.726
Industry (belong to secondary industry)	0.115	0.389	0.303	0.502	1.309
<b>Tertiary Industry</b>	2.850	3.180	2.380	3.590	12

Table 5. Economic benefits of water supply to residentialliving of Huzhou city on project of water diversion fromYangtze River to Taihu Lake, 2002–2005Unit: 10<sup>8</sup> Yuan<sup>3</sup>.

Year	2002	2003	2004	2005	Total
Residential Living	0.039	0.131	0.098	0.147	0.415

Table 6. Statistical results on total volume of water use and structure of gross domestic product in Huzhou city.

Year	Total volume of water (billion m <sup>3</sup> )	Value-added of Primary Industry (%)	Value-adde d of Indus- try (%)	Value-added of Tertiary Industry (%)
2002	1.804	12.2	46.6	34.2
2003	1.764	11.3	46.7	35.4
2004	1.841	11	47.8	34.2
2005	1.776	9.8	48.8	35.25

Source: 2005 Huzhou Statistical Yearbook, P. R. China [7] and Huzhou Water Resources Bulletin, P. R. China (2002–2005) [14].

Table 7. Results of grey relation analysis method.

Item	Grey Relation Degree of Structure of Gross Domestic Product				
	Primary Industry	Industry	Tertiary Industry		
Grey rela- tion degree	0.7372	0.5697	0.8068		
Weight	0.3488	0.2695	0.3817		

had a higher accuracy than the linear single regression model. Lin *et al.* [13] used GRA to analyse the productivity, aggregate energy consumption, and the use of fuel mix in relation to  $CO_2$  emission changes and thus the suggestions are given.

According to the grey relation analysis method, the total volume of water use were considered as main element sequence, and the structure of gross domestic product was thought as sub-element sequences (see Table 6). The computational results are listed in Table 7.

From Table 7, the grey relation degree of value-added of tertiary industry is the highest, reaching the value of 0.8068, while that of industry is the lowest with the value of 0.5697. Thus, adding the water supply can greatly improve the value-added of tertiary industry.

#### 6. Conclusions

The paper has developed an analytical research framework on benefits of water supply to Huzhou city on the project of water diversion from Yangtze River to Taihu Lake. The result is perfectly coincident with that of the grey relation degree analysis method. It also showed that the project of water diversion from Yangtze River to Taihu Lake plays an important role in improving economic benefits to Huzhou city. It also proves significant and necessary to continuously implement water diversion from Yangtze River to Taihu Lake.

However, in the paper, only direct economic benefits of water supply to Huzhou city on the project of water diversion from Yangtze River to Taihu Lake were calculated by analyzing the value-added of water supply. It is insufficient in researching ecological and social benefits, such as zoology, environment, health and physiology etc., with water improvement and water flow changes resulting from the increase of value-added of water supply. The future research will focus on the ecological and social benefits of the project.

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