Advances in Chemical Engineering and Science, **2011, 1, 77-82**
doi:10.4236/aces.2011.12013 Published Online April 2011 (http://www.scirp.org/journal/aces)

Amphiphilic Block Copolymer for Adsorption of Organic Contaminants

Jae-Woo Choi[1], Kyung-Youl Baek[2], Kie-Yong Cho[2], Natalia Valer'yevna Shim[1,3], Sang-Hyup Lee[1]*
[1]*Water Environment Center*, *Korea Institute of Science and Technology*, *Seoul*, *South Korea*
[2]*Hybrid Materials Research Center*, *Korea Institute of Science and Technology*, *Seoul*, *South Korea*
[3]*University of Science and Technology*, *Daejeon*, *South Korea*
E-mail:*yisanghyup@kist.re.kr*
Received December 24, 2010; *January* 16, 2011; *accepted April* 2, 2011

Abstract

In this study, new polymeric adsorbents, 2 types of polystyrene-block-poly (N-isopropylacrylamide) (PSN, structure of hydrophobic core and hydrophilic shell), were developed and applied for removal of organic pollutants from wastewater. Encapsulation of organic pollutants by the polystyrene-block-poly (N-isopropylacrylamide) (PSN) resulted in increasing hydrophobicity of the polystyrene with abundant hydrophobic spaces within the amphiphilic block copolymer. The encapsulation mechanism of BTEX by PSN was investigated and found to be mainly attributable to the Van der Waals interactions between the aromatic ring of BTEX and the hydrophobic core of PSN. Polystyrene-block-poly (N-isopropylacrylamide) showed good potential as a novel and cost effective adsorbent for application to wastewater treatment, which can be simply regenerated and reused using an external temperature changing system.

Keywords: BTEX, Encapsulation, External Temperature Changing System, Polymeric Adsorbent, Van der Waals Force

1. Introduction

Organic contaminants naturally persist in the environment, biodegrade slowly, cause significant damage to natural water systems and consequently present problems to human health. To remove such toxic organic substances, water treatment methods such as adsorption, biodegradation, chemical oxidation (using agents such as ozone, hydrogen peroxide or chlorine dioxide), incineration and solvent extraction have been studied. Among these practical methods, adsorption has been widely used as an effective method for removal of organic contaminants from wastewater. Various adsorbents, including activated carbon, natural materials and organoclays, have been investigated for removal of organic contaminants [1-11]. Although activated carbon has high capacity of absorbing toxic organic substances and can be easily modified by chemical treatment to increase its adsorption capacity, it also has several disadvantages [12,13]. Powdered activated carbon is hard to separate from an aquatic system when it becomes exhausted or the effluent reaches the legal discharge level. Furthermore, the regeneration of exhausted activated carbon by chemical and thermal procedures is also expensive and leads to loss of the adsorbent [14-16]. In addition, biodegradation, chemical oxidation and incineration treatments become exceedingly expensive when low effluent concentrations are required, and produce by-products that can also cause pollution. Solvent extraction is also expensive and may lead to contamination of groundwater. Therefore, alternative advanced technologies have to be investigated, and polymer adsorbents offer advantages over traditional carbon adsorbents since they can be simply regenerated by washing with a chemical solution, such as acid or alkali, under ambient conditions [17-19].

In this study, new polymeric adsorbents, 2 types of polystyrene-block-poly (N-isopropylacrylamide) (PSN, structure of hydrophobic core and hydrophilic shell), were developed and applied for the removal of organic pollutants from wastewater. When this novel material is discharged into water, micelles form as a unit molecule. Through hydrophobic binding, the core-organic com-

plexes are effective in adsorbing a variety of organic pollutants from water. It was found that the total mole cular weight of the PSN and the hydrophobic to hydrophilic ratio influenced the encapsulation and removal of BTEX from wastewater.

2. Materials and Methods

2.1. Chemicals and Materials

Carboxyl acid group terminated trithiocarbonate as a chain transfer agent (CTA) and polystyrene-block-poly (N-isopropylacrylamide) (PSN) as an adsorbent were synthesized by previously reported literature (**Figure 1**) [20]. Chemicals used for BTEX encapsulation experiment were benzene, toluene, ethylbenzene, xylene and methanol, all of them were reagent grade and purchased from Sigma-Aldrich.

2.2. Polystyrene-Block-Poly (N-Isopropylacrylamide) Analysis

Polystyrene-block-poly (N-isopropylacrylamide) was characterized via size exclusion chromatography (SEC), comprised of a Shodex GPC LF-804 column, CTS 30 column oven, Youngrin refractive index (RI) detector and HITACHI L-6000 pump, with dimethylformaide (DMF) used as the eluent, at a flow rate of 1.0 ml/min, to analyze for the molecular weight and polydispersity index (PDI). Thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to measure the weight changes as a function of the temperature and the temperatures and heat flows associated with thermal transitions in the polystyrene-block-poly N-isopropylacrylamide), respectively. The conditions used for the TGA and DSC were temperature ranges of 27 - 1000℃ and –70 - 600℃, respectively, with a sensitivity and heating rate of 0.5 - 100 mcal/sec and 0.1 - 200℃/min, respectively.

2.3. Encapsulation Procedure

The encapsulation reaction was carried out in 25 ml screw-cap vials, with Teflon-backed septa, and stirred on a rotary shaker. Sample aliquots of 1 ml were withdrawn from the reactor at regular time intervals using a syringe. Multiple experiments were carried out for a given set of conditions. Preliminary experiments indicated that the adsorption equilibrium of BTEX was reached at around 24 h, with no appreciable decrease in the adsorbate bulk concentration for time periods of up to 2 days. Controlled experiments, where there were no reactions with the adsorbents, were also conducted to confirm that the decreases in the BTEX concentrations were actually caused by adsorption onto the adsorbents rather than by adsorption onto the walls of the glass bottles or from volatilization.

2.4. Encapsulation Analysis

BTEX standards; 20, 10, 5, 1 and 0.1 $mg \cdot L^{-1}$, were prepared in deionized water (18 MΩ·cm) by diluting a 1000 $mg \cdot L^{-1}$ BTEX solution prepared in methanol. Replicate aliquots of 1 ml were placed in 10 ml Teflon-sealed screw-caps vials for GC analysis. The standard solutions were also run to check for the effects. Separate standard solutions of benzene, toluene, ethylbenzene and xylene; 20, 10, 5, 1 and 0.1 $mg \cdot L^{-1}$, were also prepared for GC analyses by appropriate dilution of 1000 $mg \cdot L^{-1}$ solutions of each compound. Glass bottle experiments were carried out by bringing 10 ml aliquots of the stock solution into contact with 20 $mg \cdot L^{-1}$ for each BTEX solution and 0.05 g of each adsorbent polystyrene-block-poly (N-isopropylacrylamide) (PSN) in glass bottles sealed with Teflon- sealed screw-caps. The bottles were then shaken for 24 h on a temperature controlled shaker at 20℃ to attain equilibrium. Gas chromatograph (Varian STAR 3400 CX; Purge & Trap) equipped with a flame ionization detector (FID) was used for analysis of the equilibrium concentration.

3. Results and Discussion

3.1. Polystyrene-Block-Poly (N-Isopropylacrylamide) Characterization

In this study, 2 types of polystyrene-block-poly (N-iso-

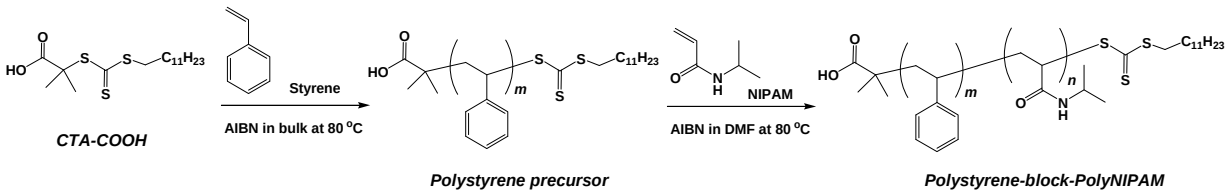

Figure 1. Synthesis of polystyrene-block-poly(N-isopropylacrylamide) (PSN), using the situational reversible addition fragmentation chain transfer polymerization (RAFT) of styrene and N-isopropylacrylamide, from the carboxyl acid group terminated trithiocarbonates and AIBN initiating system.

propylacrylamide) (PSN) were synthesized for application to the encapsulation of BTEX compounds in aqueous phase. The molecular weight (M_w), weight percent (W_t) and poly dispersity index (PDI) values of each PSN are presented in **Table 1**. The well-defined amphiphilic block copolymers obtained with relatively narrow molecular weight distributions (PDI < 1.2). PSN 01 and PSN 02 had different polystyrene M_w, but the M_w of PSN with almost the same as the W_t of P-NIPAM (Poly-N-isopropylacrylamide). The amount of polystyrene is critical, as styrene is hydrophobic, and allows for enlarged encapsulation room, which influences the capacity for BTEX removal. In addition, the W_t of PNIPAM is significant because N-isopropylacrylamide makes to solubilized the PSN polymer and introduce the PSN polymer to LCST (Low Critical Solution Temperature) system.

The TGA and DSC curves for adsorbent, polystyrene-block-poly (N-isopropylacrylamide) and the pure adsorbent resulting from the RAFT (Reversible Addition Fragmentation chain Transfer) polymerization, are shown in **Figure 2**. According to the TGA curve, an abrupt weight decrease about 94.8% was occurred within 397 to 436˚C and the polystyrene-block-poly (N-isopropylacrylamide) was almost volatilized about 99.6% at 870℃. In temperature range 67.5 to 108.1˚C, the PSN had a heat capacity about 138.1 $J \cdot g^{-1}$, as shown in **Figure 2**. This means that the PSN is very stable below 67˚C and can be recovered using an external temperature changing system (32˚C) after BTEX treatment. This thermal characteristic of PSN allows to be easily and safely separated of encapsulated BTEX.

3.2. Encapsulation Studies-Removal Capacity of BTEX

When PSN is discharged into water, it forms micelles as unit molecules (**Figure 3**). In the adsorption mechanism of aromatic compounds existed in the liquid phase into the PSN, the main type of interactions are Van der Waals forces. The hydrophobic core activated the linked adsorptive aromatic ring and localizes its hydrophobic interaction. The encapsulation of BTEX by the polystyrene-block-poly (N-isopropylacrylamide) was slow during the initial 12 h and reached an equilibrium state after 24 h. **Figure 4** shows the equilibrium concentration after BTEX encapsulation treatment using the PSN series. For PSN 01, BTEX encapsulation was effective in the order benzene > toluene > ethylbenzene > xylene. This trend was in agreement with the molecular weights of BTEX compounds (benzene < toluene < ethylbenzene < xylene). This suggested that smaller molecules are more easily encapsulated into the hydrophobic vacancy. The similar results were shown to another recent research [21,22].

Table 1. Characterization of polystyrene-block-poly (N-isopropylacrylamide).

	M_w of PS	PDI of PS	M_w of PSN	PDI of PSN	W_t (%) of PNIPAM
PSN01	4,560	1.14	48,000	1.36	82.9
PSN02	23,900	1.13	31,800	1.42	82.1

*PS: Polystyrene; **PNIPAM: Poly(N-isopropylacrylamide); ***PSN: Polystyrene-block-poly(N-isopropylacrylamide); ****M_w: Molecular weight; *****W_t: Weight percent; ******PDI: Polydispersity Index.

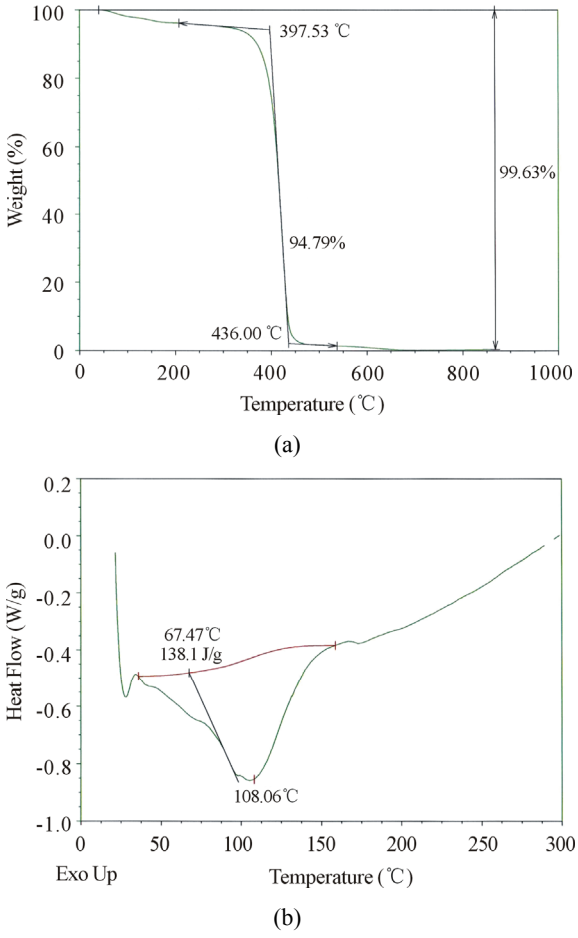

Figure 2. TGA(a)/DSC(b) curves of polystyrene-block-poly (N-isopropylacrylamide).

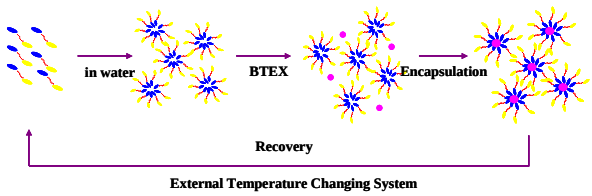

Figure 3. Efficient BTEX encapsulation and recovery mechanism using polystyrene-block-poly (N-isopropylacrylamide).

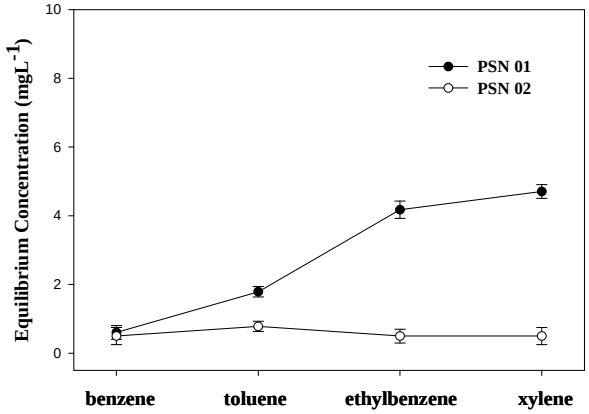

Figure 4. The equilibrium concentration after BTEX encapsulation treatment by the polystyrene-block-poly (N-isopropylacrylamide).

All the equilibrium concentrations on the PSN 02 adsorbents were lower than those on PSN 01. Consequently, in this study, PSN 02 was found to be a more effective adsorbent than PSN 01 for equilibrium concentrations of all BTEX compounds via encapsulation. The amount of encapsulation, distribution ratio and percent removal, q_e (mg·g^{-1}), K_D (mL·g^{-1}) and R (%) in equilibrium concentration, respectively, were calculated as follows:

$$q_e = (C_0 - C_e) \times V/M \quad (1)$$

$$K_D = (C_0 - C_e)/C_e \times V/M \quad (2)$$

$$\%R = (C_0 - C_e)/C_0 \times 100 \quad (3)$$

where, C_0 is the initial concentration of the BTEX solution (mg·L^{-1}), C_e the equilibrium concentration of BTEX (mg·L^{-1}), V the volume of BTEX solution (l) and M the mass of PSN adsorbent (g). In **Table 2**, the sequence of distribution ratio is PSN 02 > PSN 01, which is related to the M_w of PS (23 900 > 4 560). Conversely, the order of removal capacity for the tested polymers was PSN 02 < PSN 01, and was dependent on the M_w of PSN (31 800 < 48 000). The result indicates that an amphiphilic block copolymer with a lower polystyrene molecular weight and higher PSN molecular weight would have a greater binding affinity. In other words, the Van der Waals interactions between the aromatic ring of BTEX compounds and the hydrophobic core of PSN contribute to the encapsulation of BTEX into polymer.

3.3. Encapsulation Studies-Competition in Mixed BTEX Solution

Solutions containing either a single compound and mixed compounds were analyzed to verify the difference for amounts of encapsulation. Different results were observed and it became possible because of competition between the different organic compounds within the

Table 2. Values of equilibrium encapsulation, q_e, distribution ratio, K_D, and percent removal, R (%), by each polystyrene- block-poly (N-isopropylacrylamide).

Adsorbents	Adsorbates	q_e (mg·g^{-1})	K_D (ml·g^{-1})	R (%)
PSN 01	benzene	3.8791	6,417	97.0
	toluene	3.6421	2,035	91.1
	ethylbenzene	3.1648	757.9	79.1
	xylene	3.0588	649.9	76.5
PSN 02	benzene	< 3.9	7,800	80.5
	toluene	3.8438	4,920	80.8
	ethylbenzene	< 3.9	7,800	80.5
	xylene	< 3.8	3,800	81.0

mixture adsorbed by PSN 01 (**Figure 5**). Lesser amounts of BTEX adsorption were observed due to the competition between the BTEX within mixed solutions. The adsorption of BTEX was; thus, observed to proceed in the order xylene < ethylbenzene < toluene < benzene. The tendency for adsorption of organic chemical compounds (BTEX) is generally explained as being associated with increasing solubility and decreasing molecular weight [23,24]. For the observed uptake of BTEX, it appears that the PSN 01 amphiphilic block copolymer exhibited different removal capacities (R, %) in the order benzene > toluene > ethylbenzene > xylene (**Table 3**).

The results of present study showed that polystyrene-block-poly (N-isopropylacrylamide) is an effective adsorbent for BTEX treatment, with potential application as a novel and cost effective adsorbent for organic pollutants, which can also be simply regenerated and reused with LCST characteristics. Taking into consideration not only the encapsulation of BTEX, but also their decomposition, further works is in progress to improve the encapsulation capacity of the amphiphilic block copolymer

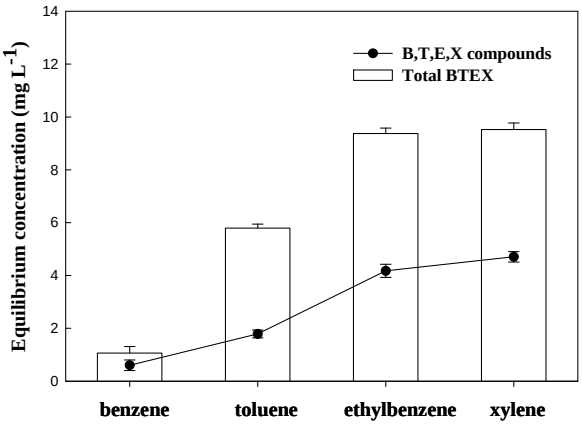

Figure 5. Equilibrium concentration after BTEX encapsulation treatment by the PSN 01 amphiphilic block copolymer.

Table 3. Different equilibrium encapsulation values, q_e, distribution ratio, K_D, and percent removal, R(%), into PSN01 when total BTEX was discharged.

	benzene	toluene	ethylbenzene	xylene
q_e (mg·g^{-1})	3.7876	2.8411	2.1251	2.0949
K_D (mL·g^{-1})	3,566	490	227	220
R (%)	94.7	71.0	53.1	52.4

and on the introduction of a photocatalytic amphiphilic block copolymer.

4. Conclusions

Novel polymeric adsorbents, 2 types of polystyrene-block-poly (N-isopropylacrylamide) (PSN), were developed and could be applied for removal of dissolved organic pollutants from wastewater. When this novel material is discharged into water, micelles form as a unit molecule. Encapsulation of organic contaminants by the polystyrene-block-poly (N-isopropylacrylamide) (PSN) resulted in increased hydrophobicity of the polystyrene, with abundant hydrophobic spaces within the amphiphilic adsorbents. This means that the core-organic complexes are effective in adsorption of various organic pollutants by hydrophobic binding. The encapsulation mechanism of aromatic compounds by PSN was investigated and found to be mainly attributable to the Van der Waals interactions between the aromatic ring of BTEX and the hydrophobic core of PSN is the main kinetics of BTEX removal. Polystyrene-block-poly (N-isopropy-lacrylamide) showed good potential as a new cost effective adsorbent for application to wastewater treatment, which can be simply regenerated and reused by changing temperature of external solution.

5. Acknowledgement

Authors acknowledge that this study was granted by project No 022-081-044 from the Next-generation Core Environmental Technology Development Project by the Ministry of Environment in Korea.

6. References

[1] A. Bembnowska, R. Pelech and E. Milchert, "Absorption from Aqueous Solutions of Chlorinated Organic Compounds onto Activated Carbon," *Journal of Colloid and Interface Science*, Vol. 265, 2003, pp. 276-282. doi:10.1016/S0021-9797(03)00532-0

[2] Y. Matsui, Y. Fukuda, T. Inoue and T. Matsushita, "Effect of Natural Organic Matter on Powdered Activated Carbon Adsorption of Trace Contaminants: Characteristics and Mechanism of Competitive Adsorption," *Water Research*, Vol. 37, 2003, pp. 4413-4424. doi:10.1016/S0043-1354(03)00423-8

[3] S. Nouri, F. Haghseresht and G. Q. M. Lu, "Comparison of Adsorption Capacity of p-Cresol & p-Nitrophenol by Activated Carbon in single and Double Solute," *Adsorption*, Vol. 8, 2002, pp. 215-223. doi:10.1023/A:1021260501001

[4] M. F. R. Pereira, S. F. Soares, J. J. M. Orfao and J. L. Figueiredo, "Adsorption of Dyes on Activated Carbons: Influence of Surface Chemical Groups," *Carbon*, Vol. 41, 2003, pp. 811-821. doi:10.1016/S0008-6223(02)00406-2

[5] R. Crisafully, M. A. L. Milhome, R. M. Cavalcante, E. R. Silveira, D. D. Keukeleire and R. F. Nascimento, "Removal of Some Polycyclic Aromatic Hydrocarbons from Petrochemical Wastewater Using Low-Cost Adsorbents of Natural Origin," *Bioresource Technology*, Vol. 99, 2008, pp. 4515-4519. doi:10.1016/j.biortech.2007.08.041

[6] J. M. Li, X. G. Meng, C. W. Hu and J. Du, "Adsorption of Phenol, p-Chlorophenol and p-Nitrophenol onto Functional Chitosan," *Bioresource Technology*, Vol. 100, 2009, pp. 1168-1173. doi:10.1016/j.biortech.2008.09.015

[7] T. Robinson, B. Chandran and P. Nigam, "Removal of Dyes from a Synthetic Textile Dye Effluent by Biosorption on Apple Pomace and Wheat Straw," *Water Research*, Vol. 36, 2002, pp. 2824-2830. doi:10.1016/S0043-1354(01)00521-8

[8] M. X. Loukidou, K. A. Matis and A. I. Zouboulis and M. Liakopoulou-Kyriakidou, "Removal of As (V) from Wastewaters by Chemically Modified Fungal Biomass," *Water Research*, Vol. 37, No. 18, 2003, pp. 4544-4552. doi:10.1016/S0043-1354(03)00415-9

[9] S. Y. Lee, S. J. Kim, S. Y. Chung and C. H. Jeong, "Sorption of Hydrophobic Organic Compounds onto Organoclays," *Chemosphere*, Vol. 55, 2004, pp. 781-785. doi:10.1016/j.chemosphere.2003.11.007

[10] R. Celis, H. M. Carmen and J. Cornejo, "Heavy Metal Adsorption by Functionalized Clays," *Environmental Science & Technology*, Vol. 34, 2000, pp. 4593-4599. doi:10.1021/es000013c

[11] O. Abollino, M. Aceto, M. Malandrino, C. Sarzanini and E. Mentasti, "Adsorption of Heavy Metals on Na-Montmorillonite Effect of pH and Organic Substances," *Water Research*, Vol. 37, 2003, pp. 1619-1627. doi:10.1016/S0043-1354(02)00524-9

[12] M. Kruk and M. Jaroniec, "Determination of the Specific Surface Area and the Pore Size of Microporous Carbons from Adsorption Potential Distributions," *Langmuir*, Vol. 14, 1999, pp. 1442-1448. doi:10.1021/la980789f

[13] S. Babel and T. A. Kurniawan, "Low-Cost Adsorbents for Heavy Metals Uptake from Contaminated Water: A Review," *Journal of Hazardous Materials*, Vol. 97, 2003, pp. 219-243. doi:10.1016/S0304-3894(02)00263-7

[14] M. C. Diez, M. L. Mora and S. Videla, "Adsorption of Phenolic Compounds and Color from bleached Kraft Mill Effluent Using Allophanic Compounds," *Water Research*, Vol. 33, 1999, pp. 125-130. doi:10.1016/S0043-1354(98)00161-4

[15] Z. Qinglin and T. C. Karl, "Adsorption of Organic Pollutants from Effluents of a Kraft Pulp Mill on Activated Carbon and Polymer Resin," *Advances in Environmental Research*, Vol. 3, 2001, pp. 251-258.

[16] J. H. Qu, "Research Progress of Novel Adsorption Processes in Water Purification: A Review," *Journal of Environmental Sciences*, Vol. 20, 2008, pp. 1-13. doi:10.1016/S1001-0742(08)60001-7

[17] B. G. Broddevall, "Purification of Wastewater from sulphate Pulp Bleaching Plants," US Patent 3, 969,990, 1976.

[18] A. K. Chowdhury, "Process for Treatment of Caustic Liquors," US Patent 4, 350, 599, 1982.

[19] A. A. Atia, A. M. Donia, S. A. Abou-El-Enein and A. M. Yousif, "Studies on Uptake Behavior of Copper(II) and Lead(II) by Amine Chelating Resins with Different Textural Properties," *Separation and Purification Technology*, Vol. 33, 2003, pp. 295-301. doi:10.1016/S1383-5866(03)00089-3

[20] J. T. Lai, D. Filla and R. Shea, "Functional Polymers from Novel Carboxyl-Terminated Trithiocarbonates as Highly Efficient RAFT Agents," *Macromolecules*, Vol. 35, 2002, pp. 6754-6756. doi:10.1021/ma020362m

[21] L. Tušek, K. Stana-Kleinschek, V. Ribitsch and S. Strnel, "Spectrophotometric and Electrokinetic Characterization of Dye Sorption on PA6," *Materials Science Forum*, Vol. 456, 2004, pp. 455-458. doi:10.4028/www.scientific.net/MSF.455-456.455

[22] M. Marsili, N. Witkowski, O. Pulci, O. Pluchery, P. L. Silvestrelli, R. Del Sole and Y. Borensztein, "Adsorption of Small Hydrocarbon Molecules on Si Surfaces: Ethylene on Si(001)," *Physical Review B*, Vol. 77, 2008, pp. 125337-125344. doi:10.1103/PhysRevB.77.125337

[23] F. DeSilva, "Acrivated Carbon Filtration," *Water Quality Products Magazine*, 2000.

[24] L. K. Wang, R. P. Leonard, D. W. Goupil and M. H. Wang, "Adsorption of Dissolved Organics from Industrial Effluents on to Activated Carbon," *Journal of Chemical Technology and Biotechnology*, Vol. 25, 2007, pp. 491-502.

