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Assessment of Surfactant Modified Activated Carbon for Improving Water Quality

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Abstract

Effluents containing inorganic contaminants are releasing into the environment untreated despite being hazardous to man and environment. It is costly and unsustainable to use conventional methods to remove them from dilute aqueous solution. Adsorption involving granular activated carbon is an alternative method for treating such effluents. Granular activated carbon is structurally strong, highly resistance to attrition and wearing, large and can easily separate from the effluents. However, its surface is highly hydrophobic and has little surface charge thereby reducing its adsorption capacity for anion or cation. This article reviews surfactant modification of activated carbon to enhance its adsorption capacity for inorganic contaminants and key factors affecting the adsorption efficiency. They include initial concentration of contaminants, contact time, solution pH, solution temperature, adsorbent concentration, ionic strength, competing ions, type of surfactant, and surfactant concentration. The modified activated carbon usually shows maximum contaminant uptake around its critical micelles concentration. Surfactant modification reduces specific surface area and/or micro pore volume but hot NaOH or HNO_3 treatment before surfactant modification minimises this drawbacks and increases the net surface charge. Overall, surfactant modification is a simple but efficient method of enhancing adsorption capacity of activated carbon for removing anion or cation from aqueous solution. However, a handful publication is available on the regeneration of the spent (saturated) surfactant modified activated carbons. Hence, more research efforts should be directed towards proper regenerating reagents and the optimise conditions such as contact time, concentration, and temperature for regenerating spent modified activated carbons.

Keywords

Surfactant, Modification, Adsorption, Activated Carbon, Inorganic Contaminants Regenerating

1. Introduction

Massive industrial, domestic, agricultural, medical and technological applications of heavy metals contribute to their prevalence in the environment [1]. Anionic contaminants' main sources are widely varied. Perchlorate main sources include untreated effluents containing perchlorate salts from manufacturing of matches, airbags, explosives etc. [2] [3]. Byproduct of drinking water disinfection accounts for the main source of bromate contamination [4]. Nitrate contaminates environment mainly through untreated run off from fertilizer, septic tank and sewage [4] [5] while untreated discharge from steel and pulp mills accounts for major chromium released into the environment [4] [6].

According to United State Environmental Protection Agency, National Primary Drinking Water Regulations [4] the maximum contaminant level (MCL) in primary drinking water for inorganic contaminants are: arsenic, 0.10 mg/L; cadmium, 0.005 mg/L; lead, 0.015 mg/L; chromium, 0.1 mg/L, mercury, 0.002 mg/L; bromate, 0.1 mg/L; nitrate, 10 mg/L; chromium (total), 0.1 mg/L etc. In addition, they are hazardous to human health if consumed above the stated MCL. Arsenic causes skin damage, problems with circulatory systems, increased risk of getting cancer; cadmium causes kidney damage; lead causes kidney problem and high blood pressure in adults but delays physical and metal developments in infants and children; chromium causes allergic dermatitis; mercury causes kidney problem; bromate is carcinogen; chromium causes allergic dermatitis while excess intake of nitrate above MCL could lead to death in infant if left untreated.

Despite these potential health hazards of inorganic contaminants to man and negative impact to the environment, over 80% of the wastewater globally generated and over 95% in some least developed countries is released into the environment untreated [7]. This has attracted public concerns and motivated investigations into a sustainable treatment of cations or anions containing effluents.

The conventional methods of removing water contaminants from effluents include ion exchange, evaporation, chemical precipitation, membrane separation, chemical oxidation or reduction, electrochemical treatment, reverse osmosis [8] [9] [10]. However, these methods have disadvantages including lack of specificity and ineffective at low concentration [11], fouling of membrane by slightly soluble components [12] and high cost [10] [11]. In addition they need large footprint, sludge dewatering facilities, highly skilled operators and multiple basin configurations [13].

Similarly, adsorption involving nano-adsorbents or powdered activated carbon is hardly used due to operational problems. This includes complex and costly synthesis, turbidity inducement and separation difficulty [14] [15] [16]. In contrast, granular activated carbons due to their large size and hardness can be easily separated from aqueous media, do not cause turbidity in the treated water but have relatively low specific surface area. Besides, both powdered and granular activated carbons have low adsorption capacities for inorganic (cations or

anions) contaminants due to their little active binding sites (surface functional groups) for such contaminants.

Considering the fact that activated carbon's surface is highly hydrophobic [17] [18] surfactant can be anchored on it using its hydrophobic group while its hydrophilic group tends towards the aqueous phase and ultimately determines its net surface charge [17] [19]. Modification of activated carbon with cationic surfactant makes its net surface charge positive [20] [21] [22] but using anionic surfactant makes it negative [23] [24]. In addition, keeping the pH of surfactant modified activated carbon system below or above pHpzc (pH at which its surface charge equals zero) can alter the net surface charge from positive to negative or vice versa [20] [21] [22]. This flexibility will promote regeneration of spent (saturated) modified activated carbons.

This article reviews the use of surfactant modified activated carbons for adsorption of anions or cations from aqueous solutions, environmental factors and surfactant properties required to improve the process efficiency, drawbacks of the surfactant modified activated carbon and ways to minimise them. The author also suggests areas required more research effort.

2. Applications of Surfactant Modified AC in Water Treatment

Granular activated carbon is structurally strong, highly resistance to attrition and wearing [25]. These compelling characteristics together with their large size will make them easily separated from the effluents. But they are commonly used for adsorption of organic contaminants from gaseous and/or liquid mixtures due to their large hydrophobic surface. Inorganic contaminants and heavy metals usually exist in solution as ions or hydrous ionic complex [19] making activated carbon almost less effective for removing them. One technique of enhancing activated carbon surface for adsorption of inorganic contaminants is surfactant surface modification. This approach is more appealing due to its flexibility and simplicity

2.1. Adsorption of Inorganic Contaminants

Previous investigations show that surfactant surface modification of activated carbon is possible and effective for enhancing its adsorption capacity for removing inorganic contaminant from aqueous media. **Table 1** clearly shows that percentage cation or anion removed by surfactant modified activated carbons is generally greater than unmodified (virgin) activated carbon at the same experimental conditions. This higher uptake capacity is consistent for the surfactant modified activated carbons regardless of their parent sources and whether powdered or granular.

Anh *et al.* [23] compared the specific uptake of Cd (II) ions by surfactant modified activated carbon with unmodified (virgin) one. At pH 6, initial Cd (II) concentration (100 mg/L), 20˚C and 120 min contact, the order of specific uptake obtained are sodium dodecyl sulphate (SDS) modified activated carbon,

Table 1. Effect of surfactant modification on adsorption capacity of activated carbon.

Contaminant	Surfactant, concentration. (g/L)	Solution pH	Initial conc. or range (mg/L)	Contact time (min)	Agitation (rpm)	Temp. (˚C)	Kinetic model	Isotherm	Contaminant removed (% or mg/g)	References
Cd (II)	SDS, 10.1, 4.28*CMC	6	100	120	100	20	Pseudo second order	Freundlich	22.3	Ahn *et al.* [23]
	SDBS, 10.1 10.64*CMC	6	100	120	100	20	Pseudo second order	Freundlich	17.53	Ahn *et al.* [23]
	DSS, 10.1 5.94*CMC	6	100	120	100	20	Pseudo second order	Freundlich	17.31	Ahn *et al.* [23]
	Virgin activated carbon	6	100	120	100	20	Pseudo second order	Freundlich	2.47	Ahn *et al.* [23]
Cd (II)	SDBS, 30.7 73.4*CMC	4.5 - 7.2	10 - 100	1440	-	25	–	Langmuir	44.2[a]	Sun *et al.* [24]
	Virgin activated carbon	4.5 - 7.2	10 - 100	1440	-	25	–	Langmuir	6.8	Sun *et al.* [24]
Co (II)	SDS, 3.54 1.5*CMC	7	20 - 100	90	250	40	Pseudo second order	Langmuir	51	Kakavandi [26]
Bromate	CTAC, 0.64 1.26*CMC	3	2 - 20	1440	-	25	Pseudo second order	Langmuir	38.02	Chen *et al.* [25]
	Virgin activated carbon	3	2 - 20	1440	-	25	Pseudo second order	Langmuir	7.02	Chen *et al.* [25]
Bromate	CTAC, 0.64 2*CMC	-	1 - 100	720	-	-	Pseudo second order	Langmuir	35.8	Farooq*et al.* [22]
	CPC, 0.68 2*CMC	-	1 - 100	720	-	-	Pseudo second order	Langmuir	34.2	Farooq*et al.* [22]
Bromate	CTAB, 0.729 2*CMC	-	1 - 100	720	-	-	Pseudo second order	Langmuir	13.1	Farooq *et al.* [22]
	Virgin activated carbon	-	1 - 100	720	-	-	Pseudo second order	Langmuir	~13.1	Farooq *et al.* [22]
Nitrate	CTAB, 10.9 33.3*CMC	5.6	100	5	250	25	Pseudo second order	Langmuir	83.3; 60%	Allalou*et al.* [28]
	Virgin activated carbon	5.6	100	5	250	25	Pseudo second order	Langmuir	14%	Allalou *et al.* [28]
Nitrate	CTAB, 0.164 0.5*CMC	7	40 - 200	120	200	25	Pseudo second order	Langmuir	21.5[b]	Mazarji *et al.* [27]
Nitrate	CPMG, 2.5	6.5 - 6.8	25 - 376	90	150	23	Pseudo second order	Langmuir	26	Cho *et al.* [29]
	Virgin activated carbon	6.5 - 6.8	25 - 376	90	150	23	Pseudo second order	Langmuir	14.3	Cho *et al.* [29]
Cr (VI)	CPMG, 2.5	6.5 - 6.8	25 - 376	90	150	23	Pseudo second order	Langmuir	81	Cho *et al.* [29]
	Virgin activated carbon	6.5 - 6.8	25 - 376	90	150	23	Pseudo second order	Langmuir	55	Cho *et al.* [29]
Cr (VI)	HDTMA, 0.168 0.5*CMC	-	10 - 200	180	150	20	Pseudo second order	Langmuir	4.06	Choi *et al.* [17]
	CPC, 0.161 0.5*CMC	-	10 - 200	180	150	20	Pseudo second order	Langmuir	3.70	Choi *et al.* [17]
	Virgin activated carbon	-	10 - 200	180	150	20	Pseudo second order	Langmuir	1.28	Choi *et al.* [17]
Perchlorate	CTAC, 1.6 5*CMC	~6.7	5 - 50	120	120	60		Langmuir	55.3	Tang *et al.* [21]

[a]Treatment with HNO_3 before SDBS modification; [b]Treatment with NaOH before CTAB modification.

22.3 mg/g > sodium dodecyl benzene sulfonate (SDBS) modified activated carbon, 17.53 mg/g > dioctyl sulfocuccinate sodium (DSS) modified activated carbon, 17.31 mg/g > virgin activated carbon, 2.47 mg/g. Similarly, Kakavandi *et al.* [26] observed enhancement in specific uptake of Co (II) ions by SDS modified activated carbon reaching a maximum specific uptake of 51 mg/g.

Sun *et al.* [24] worked on HNO_3/SDBS/activated carbon system for adsorption of Cd (II) ion from aqueous solution. The specific Cd (II) ion uptake obtained are HNO_3–SDBS modified activated carbon, 44.2 mg/g > SDBS modified activated carbon, 26.6 mg/g > HNO_3 modified activated carbon, 22.8 mg/g >virgin activated carbon, 6.78 mg/g at optimum modification conditions: HNO_3 concentration (3.29 mol/L), SDBS concentration (30, 700 mg/L) and 76˚C. HNO_3 was used to treat the activated carbon before SDBS modification.

Surfactant modified activated carbons equally work effectively for enhancing adsorption of anions from aqueous solutions. Chen *et al.* [25] compared the adsorption capacity of cetyltrimethyl ammonium chloride (CTAC) modified activated carbon with virgin activated carbon for bromate uptake from aqueous solution. They observed CTAC modified activated carbon produced specific bromate uptake of 38 mg/g which was greater than 7.02 mg/g for the virgin activated carbon. Similarly, bromate specific uptake observed by Farooq *et al.* [22] are CTAC modified activated carbon, 35.8 mg/g > cetylpyridinium chloride (CPC) modified activated carbon, 34.2 mg/g > cetyltrimethylammonium bromide (CTAB) modified activated carbon, 13.1 mg/g >virgin activated carbon, ~13 mg/g at 12 h contact.

Other researchers reported enhancement in percentage nitrate removed by CTAB modified activated carbon [27] [28] and percentage perchlorate removed by CTAC modified activated carbon [21] compared with virgin activated carbon.

Cho *et al.* [29] has shown the possibility of enhancing adsorption capacity of activated carbon for nitrate and Cr (VI) from aqueous solution using quaternary ammonium-containing polymer. They observed that the cationic [3–(methacryloylamino)propyl]–trimethylammonium chloride modified activated carbon (CPMG) has specific nitrate uptake of 26 mg/g which was greater than 14.3 mg/g obtained for the virgin activated carbon. For Cr (VI), specific uptake of 81 mg/g was recorded for the modified activated carbon compared to 55 mg/g obtained for the virgin activated carbon.

Table 1 shows that that pseudo second order rate model properly describes the adsorption kinetic data of the modified activated carbons. Langmuir adsorption isotherm commonly fit properly the equilibrium adsorption data than the Freundlich isotherm for inorganic ions (cations and anions) adsorption onto the surface of surfactant modified activated carbons.

Table 2 clearly shows that surfactant modification causes reduction in BET specific surface area and/or micro pore volume. This is due to pore blockage as the surfactant anchors its hydrophobic group onto the activated carbon via the micropores. Allalou *et al.* [28] observed that a virgin activated carbon with initial

Table 2. Effect of pre-treatment and surfactant modification on the surface area and pore volume.

Surfactant	Virgin activated carbon		Pre-treated activated carbon		Modified activated carbon		References
	BET specific surface area (m^2/g)	Micropore volume (cm^3/g)	BET specific surface area (m^2/g)	Micro pore volume (cm^3/g)	BET specific surface area (m^2/g)	Micropore volume (cm^3/g)	
CTAB	888	0.376	901[a]	0.400[b]	722[c]	0.310[d]	Mazarji *et al.* [27]
SDBS	158.1	0.0804	185.07[e]	0.0937[f]	131.4[g]	0.0729[h]	Sun *et al.* [24]
CTABr	1407	-	-	-	608.9	-	Allalou *et al.* [28]
CPC	822.7	-	-	-	608.9	-	Farooq *et al.* [22]
CTAB	822.7	-	-	-	600.1	-	Farooq *et al.* [22]
CTAC	822.7	-	-	-	571.3	-	Farooq *et al.* [22]

[a]BET specific surface area after NaOH treatment, [b]Micropore volume after NaOH treatment, [c]BET specific surface area after NaOH treatment plus CTAB modification, [e]BET specific surface area after HNO_3 treatment, [f]Micropore volume after HNO_3 treatment, [g]BET specific surface area after HNO_3 treatment plus SDBS modification, [h]Micropore volume after HNO_3 treatment plus SDBS modification.

BET specific surface of 1407 m^2/g reduced to 569 m^2/g after CTAB modification. Similarly, Farooq *et al.* [22] observed that a virgin powdered activated carbon (PAC) with initial 822.7 m^2/g BET specific surface area reduced to 608.9 m^2/g, 600.1 m^2/g and 571.3 m^2/g respectively after modification with CPC, CTAB and CTAC.

However, treatment with NaOH or HNO_3 prior to surfactant modification has been shown to minimise the reduction in the BET specific surface surface or micro pore volume and ultimately increase the net surface charge of the modified activated carbons. Mazarji *et al.* [27] recorded that the BET specific surface area and micro pore volume of a virgin activated carbon, 888 m^2/g and 0.376 cm^3/g increased to 901 m^2/g and 0.400 cm^3/g respectively after NaOH treatment but slightly reduced to 722 m^2/g and 0.310 cm^3/g after CTAB modification of the NaOH treated activated carbon. They obtained percentage nitrate removal of NaOH–CTAB modified activated carbon, 80%, >NaOH–pre-treated activated carbon, 16% > virgin activated carbon, 8%.

Similarly, Sun *et al.* [24] observed that the BET specific surface area and micro pore volume of a virgin activated carbon, 158 m^2/g and 0.0804 cm^3/g increased to 185.07 m^2/g and 0.0937 cm^3/g respectively after HNO_3 treatment but reduced to 131.4 m^2/g and 0.0729 cm^3/g after SDBS modification. They obtained specific Cd (II) uptake with HNO_3–SDBS modified activated carbon, 44.2 mg/g > SDBS modified activated carbon, 26.6 mg/g > HNO_3 modified activated carbon, 22.8 mg/g > virgin activated carbon, 6.78 mg/g. The modified and activated carbons' performances seems to follow the same order as the net surface charge with HNO_3–SDBS modified activated carbon, −39.7 > HNO_3 modified activated carbon, −28.1 > SDBS modified activated carbon, −22.1 > virgin activated carbon, −18.6. Although there was an interchange in place between HNO_3 modified activated carbon and SDBS modified activated carbon, nevertheless combination of HNO_3 treatment with SDBS modification resulted into an increase in the net surface charge of the virgin activated carbon and enhancement in the adsorption capacity.

2.2. Sorption Mechanism of Surfactant Modified Activated Carbon

Surface characterisation of virgin activated carbons shows that they have functional groups including carboxyl (R–COOH), phenolic (R–OH) and carbonyl (R = O) [23] [24]. The carbonyl group can complex with inorganic contaminant while the deprotonated acidic functional group can bind heavy metals ions. The possible mechanisms for anionic, SDS surfactant modified activated carbon used to remove bivalent cations from aqueous solution are as follows [23].

$$2\mathrm{ROH} + \mathrm{M}^{2+} \leftrightarrow (\mathrm{RO})_2\,\mathrm{M} + 2\mathrm{H}^+ \tag{1}$$

$$2\mathrm{RCOOH} + \mathrm{M}^{2+} \leftrightarrow (\mathrm{RCOO})_2\,\mathrm{M} + 2\mathrm{H}^+ \tag{2}$$

$$2\mathrm{RSO_3Na} + \mathrm{M}^{2+} \leftrightarrow 2\mathrm{RSO_3M} + 2\mathrm{Na}^+ \tag{3}$$

$$\mathrm{RSO_3Na} + \mathrm{H}^{2+} \leftrightarrow \mathrm{RSO_3H} + \mathrm{Na}^+ \tag{4}$$

Equation (1) and Equation (2) indicate that cations can bind with little active binding groups present originally on the virgin activated carbon if they are not covered by the surfactant after modification. Equation (3) indicates that cations can bind with negatively charged group of the anionic surfactant anchored onto the surface of the activated carbon (ion exchange). Equation (4) indicates possible competitive or inhibition binding between cations and hydrogen ions with negatively charged group of the anionic surfactant.

Possibility of these reactions is further supported by the pH profile observed by Ahn *et al.* [23] during Cd (II) adsorption by surfactant modified and unmodified activated carbons. In the initial stage of the process there was a rapid drop in the pH of the system but the pH decrease in the virgin activated carbon system was greater than that of the surfactant modified activated carbon system. Similarly, the total acidity value obtained was: virgin activated carbon, 212.5 μeq/g > SDS modified activated carbon, 125 μeq/g or SDBS modified activated carbon, 125 μeq/g > DSS modified activated carbon, 176.8 μeq/g. The decrease in the total acid was attributed to the surfactant coverage of the original functional groups on the virgin activated carbon.

Sun *et al.* [24] also observed total acidity of virgin activated carbon with 0.55 mmol/g decreased to 0.45 mmol/g after SDSB modification. Of note is that HNO_3 treatment of the virgin activated carbon increased its total acidity to 1.26 mmol/g as expected due to introduction of more acidic functional group. Then subsequent modification with SDBS reduced the total acidity to 1.03 mmol/g. This suggests that the acidic functional groups of the activated carbons were being deprotonated (dissociated) in water (Equation (1) and Equation (2)). Then, they observed a slight increase in the pH as the sorption continued. This could be due to binding of the protons onto the hydrophilic head group of anionic surfactant as shown in Equation (4) while Equation (3) confirms the increase in the specific uptake of Co (II) as contact time increased.

Possible adsorption mechanism for the uptake of anions by cationic modified activated carbons can also be made from empirical findings. Farooq *et al.* [22]

reported that the amount of chloride ions, Cl^- released by each of CPC– and CTACmodified activated carbonsafter the adsorption experiment deducted by the amount of chloride ions naturally released by each of them in the control experiments (only water) equals to bromate ions, Bro_3^- removed by each of the modified activated carbons. This suggests that ion exchange is the main mechanism of adsorption of bromate ion, Bro_3^- onto them. In contrast, the bromide ion, Br^- released by the CTAB modified activated carbon wasslightly lower than the bromate, Bro_3^- removed suggesting that the bromate removed in this system was partly by ion exchange and other mechanism such electrostatic interaction or surface complexation. Chen *et al.* [25] observed that chloride ions released by a CTAC modified activated carbon equals to 60% - 83% of bromate removed.

Sometimes amount of counter anions exchanged varies with the initial concentration of the targeted anions. Tang *et al.* [21] reported that amount of chloride ions, Cl^- released by CTACmodified activated carbon increased from 66 to 92% of perchlorate (ClO_4^-) removed as perchlorate initial concentration increased from 0.1 to 0.4 mmol/L. Similarly, Xu *et al.* [20] observed that chloride ion, Cl^- released by CTACmodified activated carbon was 47% of perchlorate (ClO_4^-) removed when perchlorate initial concentration was 0.0816 mmol/L. Then increased to 77% of perchlorate (ClO_4^-) removed as the initial perchlorate ranged from 0.1632 - 0.4897 mmol/L. This suggests that ion exchange change from minor to main mechanism as the initial concentration of the targeted anions increased. And that other mechanism such as electrostatic attraction, physical adsorption or surface complexation possibly occurred along with ion exchange.

Overall, mechanisms of adsorption of cation (anion) onto activated carbon modified by anionic (cationic) surfactant include ion exchange, electrostatic attraction, physical adsorption or surface complexation depending on the quantity, activity and masking of the surface functional groups originally present on the virgin activated carbon before surfactant modification.

3. Factors Affecting Efficiency of Surfactant Modified Activated Carbon

Factors affecting percentage ion removed and/or specific ion uptake by surfactant modified activated carbon can be broadly categorised into environ mental factors and surfactant properties.

3.1. Environmental Factors

The environmental factors include process parameters such as initial concentation of contaminants, contact time, solution pH, solution temperature, adsorbent concentration, ionic strength and competing ions.

3.1.1. Solution pH

The pH of the sorbate solution is one of the key parameters affecting adsorption.

It influences the net surface charge of the binding sites, solution chemistry of the target metal in terms of hydrolysis or complexation [30]. pH of the solution also contributes to metal precipitation, speciation and its availability for adsorption [31]. Isoelectric point pH (pH_{IEP}) or point of zero charge (pH_{PZC}) is a useful guide to find an ideal pH for maximum inorganic contaminant uptake. This is the pH of the solution at which the net surface charge on the adsorbent equals zero. Solution pH above pH_{PZC} makes the net surface charge on the adsorbent negative while solution pH below pH_{PZC} makes the net surface charge positive [32]. Electrokinetic studies to estimate the isoelectric point pH (pH_{IEP}) is documented in the literature [33] [34].

The value of the zeta potential is used to characterise the net surface charge on an adsorbent. Positive zeta potential indicates positive net surface charge while negative zeta potential means negative surface charge. At every pH the zeta potential of cationic surfactant modified activated is always higher in positive value than the corresponding virgin activated carbons [20] [21] [22] while that of anionic surfactant usually higher in negative value than the corresponding virgin activated carbon [23] [35]. The zeta potential increases as the in initial concentration of cationic surfactant increases but remains constant above the critical micelle concentration of each surfactant [22].

Xu *et al.* [20] observed that perchlorate removed by virgin or CTACmodified activated carbon peaked at pH 2 - 3 corresponding to their pH_{pzc} (pH 2 for virgin activated carbon; pH 3 for CTAC modified activated carbon). Below their pH_{pzc} perchlorate specific uptake decreased as the pH decreased and above their pH_{pzc} perchlorate specific uptake decreased as the pH increased. At every pH percentage removed by CTACmodified activated carbon consistently greater than virgin activated carbon.

Tang *et al.* [21] obtained pH_{pzc} 4.3 and 4.9 respectively for virgin activated carbon and CTAC modified activated carbon. The zeta potential of the CTAC-modified activated carbon consistently higher in positive value at every pH indicating CTAC modified activated carbon has more positive surface charge than the virgin activated carbon. Within the pH 3 - 11 range studied, specific perchlorate uptake by the virgin activated carbon decreased moderately from 9.8 mg/g at pH 3 to ~7.8 mg/g at pH 11. The specific perchlorate uptake by the CTAC modified activated carbon decreased rapidly from 27.31 mg/g at pH 3 to 10.58 mg/g at pH 11. Of note is that at each pH studied specific perchlorate uptake by CTAC modified activated carbon consistently greater than the virgin activated carbon. Other researchers obtained similar results [27] [28] [29].

Increase in the net negative surface charge of both virgin and cationic surfactantmodified activated carbon as pH increases causes repulsion between the negatively charged surface and the anions; hence reducing its uptake at such high pH. In addition, the residual hydroxide ions, OH^- produced due to higher pH compete with the targeted anions for binding on the adsorbent surface, thereby reducing the amount of anions removed. As pH decreases below

pH_{pzc}, the net positive surface charge increases allowing more of the anions to be attracted onto the adsorbent surface. This usually increases the specific anions uptake by cationic modified activated carbon. However, excessive increase in the pH far below pH_{pzc} reduced specific uptake of nitrate by CTAB modified activated carbon [28] and perchlorate by CTAC modified activated carbon [20] possibly due to repulsion between the protonated anions and positively charged amines groups on the cationic modified activated carbon [36].

Anionic surfactant modification enhances the net negative surface charge of virgin activated carbons [23] [24] and its surface become more negatively charged as the pH increases. Hence, adsorption of cations by anionic surfactant modified activated carbons increases with pH due to the attraction between the negatively charged surface and the targeted cations. For instance the specific Cd (II) uptake by DSS modified activated carbon, SDBS modified activated carbonand SDS modified activated carbonrespectively at pH 2 were 0.065, 0.075, and 0.09 mmol/g but increased steadily to 0.13, 0.140 and 0.200 mmol/g at pH 6 [23]. Of note is that the uptake by each of the anionic modified activated carbonswas greater than the virgin activated carbon at every pH. This conforms to the observation of Kakavandi *et al.* [26] regarding the adsorption of Co (II) by virgin and SDSmodified activated carbon.

This behaviour was attributed partly to reduction in competition between H^+ and Cd (II) for binding on the same sites as pH increases [37] [38]. In addition, increase in the net negative surface charge of the anionic modified surfactant as the pH increases causes attraction between the targeted cation and the negatively charged surface. However, excessive high pH should be avoided to prevent precipitation of metal hydroxide [23] [26]. The danger of microprecipitation starts at pH > 5 for lead and at pH 6.7 for nickel [39]. Microprecipitation starts at pH > 6 for copper [40] [41], at pH 7 for chromium [42] and at pH > 8 for cadium [43]. Formation of such insoluble precipitate may introduce errors into adsorption results as the removal of metal ions in the presence of such precipitate is not completely through binding on the surface function groups [44]. Occurrence of desorption of anionic surfactant anchored on the activated carbon is also high at a high pH [23].

3.1.2. Initial Concentration

Percentage inorganic contaminants removed by adsorbents usually decreases as initial ion concentration increases [26] [28] [45] [46] [47]. At low concentration of contaminant the available active binding sites are more than enough while at high initial concentration the binding sites are not enough; hence the percentage adsorbed will be higher at low initial concentration due to abundant available active bind sites compared to the number of targeted ions than at high initial concentration.

In contrast, adsorption capacity usually increases with increase in initial concentration [26] [28] [47] [48] [49]. This trend is the same for both cation adsorbed onto anionic surfactant modified activated carbon and anion adsorbed

onto cationic surfactant modified activated carbon. For instance, Kakavandi *et al.* [26] observed that at pH 7, 1.2 g/L adsorbent concentration, 20˚C, 200 rpm, Co (II) specific uptake by SDS modified activated carbon increased from 16.4 to 40.8 mg/g while the percentage cation removed decreased from 98.2% to 49% as the initial Co (II) concentration increased from 20 to 100 mg/L. Similarly, Allalou *et al.* [28] recorded an increase in the specific nitrate uptake from 32 to 80 mg/g but decrease in percentage anion removed from 92% to 40% as the initial concentration increased from 100 to 600 mg/L.

For a fixed mass of adsorbent, at low initial adsorbate concentration, active binding sites are under saturated but tend towards saturation as the initial concentration increases [28]. This will make the ratio of adsorbed concentration to initial concentration decreases as the initial adsorbate concentration increases [16]. However, increase in initial concentration increases the driving force causing more adsorbate to bind onto the adsorbent. Hence, for a fixed mass of adsorbent, increase in initial concentration of adsorbate increases the specific adsorbate uptake until equilibrium is attained [26] [27].

3.1.3. Adsorbent Concentration

Surfactant modified activated carbon concentration is another important factor affecting the percentage contaminant removed and the specific contaminant uptake. At constant adsorbate concentration, increase in concentration of the adsorbent increases the percentage contaminant removed but decreases the specific contaminant uptake.

Kakavandi *et al.* [26] at constant Co (II) initial concentration, recorded an increase in Co (II) removed from 51.3% to 95% but decrease in the specific ion uptake from 38.5 to 19 mg/g as SDS modified activated carbon concentration increased from 0.4 to 1.5 g/L. Similarly, Mazarji *et al.*, [27] at constant 40 mg/L initial nitrate concentration obtained increase in percentage nitrate removed from 25% to 83% but a decrease in specific uptake from 11 to 3.3 mg/g as CTAB modified activated carbon concentration increased from 0.05 to 0.5 g/L.

Rising in percentage adsorbate could be attributed to more active binding sites and/or enhance surface area available as the adsorbent concentration increases for a fixed initial contaminant concentration [50] [51]. Reduction in the specific ion uptake with increase in adsorbent concentration could be due to unsaturation and/or lower exploitation of the active binding sites at high adsorbent concentration. In addition, at high adsorbent concentration particles are self-bound together and form aggregate; hence reduces the effective active binding sites available for adsorption. Therefore, the specific ion adsorbed reduces with increase in the adsorbent concentration [52] [53] [54].

3.1.4. Contact Time

Percentage contaminant removed and specific contaminant uptake by surfactant modified activated carbon usually increased with contact time until equilibrium. At optimum surfactant modification conditions, the adsorption capacity of the

modified activated is usually greater than that of virgin activated carbon. However, adsorption rate of such modified activated carbons has no definite pattern. Surfactant modification could increase adsorption rate [22], reduce rate [25] [29] or maintain rate [28] when compared to virgin activated carbons.

Specifically, Farooq *et al.* [22] observed a decreasing order of adsorption rate of bromate onto various adsorbents as CTAC modified activated carbon > CPC modified activated carbon > CTAB modified activated carbon ≈ virgin activated carbon. This suggests that bromate, Bro_3^- exchange may occur rapidly with chloride counter ions, Cl^- on CTAC and CPC than with bromide counter ion, Br^- on the CTAB. Besides, increase in temperature of endothermic adsorption causes increase in rate of adsorption. For instance, pseudo second order rate constant of CTAC modified activated carbon increased from 0.0125 to 0.0311 g/(mg·min) as the solution temperature increased from 15˚C to 60˚C [21].

In contrast, Chen *et al.* [25] observed a decreasing adsorption rate after surfactant modification with virgin granular activated carbon adsorption rate > CTAC modified activated carbon. Some researchers also obtained reduction in adsorption rate after modification with polymer [29]. Of note is that surfactant modification usually reduces the BET specific surface area of the modified activated carbon due to micropore blockage. Hence surface area and micro pore volume obtained by different authors after modification are different. In addition, the process parameters such solution temperature, solution pH and agitation rates used by different author differ. All these could contribute to different trends of adsorption rate observed by different authors.

Equilibrum times reported by different authors also differ. Allalou *et al.* [28] observed a rapid increase in percentage nitrate removed in the first 5 min contact. Their system attained equilibrium within 5 min of contact for both virgin activated carbon and the CTAB modified activated carbon. Similarly, specific perchlorate uptake adsorbed onto CTAC modified activated carbon increased rapidly in the first 15 min of contact accounting for 90% of the total perchlorate uptake but the equilibrium was attained in 30 min [21].

Of note is that some authors extend the contact time during isotherm studies above the equilibrium time obtained during kinetics studies. This explains a wide range (5 - 1440 min) in the contact time listed in **Table 1**. For instance, Chen *et al.* [25] system attained equilibrium around 360 min but they used 1440 min as contact time for isotherm studies perhaps to ensure the maximum uptake that can be obtained for the modified activated carbon. In practice, rapid adsorption is most desired to allow a substantial reduction in the size of the adsorption column. This will make the process more cost effective.

3.1.5. Solution Temperature

Many authors conducted adsorption of inorganic contaminant onto surfactant modified activated carbon at ambient temperature [17] [23] [25] [28] [29]. However, few studies show that temperature has moderate effect on the percentage contaminant removed or specific contaminant uptake by the modified acti-

vated carbons indicating the process is either endothermic or exothermic.

Tang *et al.* [21] observed that the specific perchlorate uptake by CTAC modified activated carbon increased from 35.5 to 55.3 mg/g as temperature increased from 25˚C to 60˚C. They obtained positive change in enthalpy (ΔH) implying the adsorption is endothermic. Negative Gibb free energy (ΔG) was obtained indicating the adsorption is spontaneous. A positive entropy (ΔS), 22 J/(mol·K) was obtained implying a net increase in randomness of perchlorate at the solid/solution interface occurred in the internal structure of the adsorbent.

Cho *et al.* [29] recorded decrease in specific uptake from 29.4 and 77.2 to 24.4 and 56.6 mg/g respectively for both nitrate and Cr (VI) as temperature increased from 25˚C to 45˚C. In addition, negative change in enthalpy (ΔH) and change in Gribb free energy (ΔG) were obtained for both ions indicating the process is exothermic and spontaneous. They also obtained a positive change in entropy (ΔS). Hence, operating such exothermic adsorption at ambient will save cost if this does not significantly reduce the adsorption rate.

3.1.6. Ionic Strength

Increase in ionic strength (NaCl concentration) suppresses ion exchange but enhances non-electrostatic (hydrophobic) attraction [55]. Hence, the net uptake of inorganic contaminant by surfactant modified activated carbons in the presence of NaCl depends on the dominant adsorption mechanism. For instance, Tang *et al.* [21] recorded a rapid decrease in specific perchlorate uptake by CTAC modified activated carbon from 24.8 to 18.4 mg/g as the NaCl concentration increased from 0 to 10 mmol/L. Further increase in NaCl concentration to 50 mmol/L caused slight reduction to 18.06 mg/g.

The rapid reduction could be explained by suppression of ion exchange between perchlorate, ClO_4^- and CTAC on the surface of CTAC modified activated carbon suggesting that the main sorption mechanism by this system is ion exchange while the slight reduction at 50 mmol/L NaCl could be explained by occurrence of non-electrostatic interaction accounting for the perchlorate adsorption at this region [55] [56]. In addition, competition between chloride ion, Cl^- and perchlorate ions, ClO_4^- for the same active binding sites on the adsorbent also contribute to the reduction in perchlorate adsorption with increase in ionic strength [56].

There is also an interaction between NaCl concentration and the contact timeon suppression of ion uptake by the surfactant modified activated carbon. Xu *et al.* [20] in the first 60 min of contact obtained increase in specific perchlorate uptake from 1.34 to 1.80 mg/g as the ionic strength increased from 0 to 1.71 mmol/L. Further increase in ionic strength to 8.55 mmol/L decreased the specific uptake to 1.54 mg/g. The inhibition became significant at 120 min contact making the adsorption rate decreased from 46.35 g/(mmol·h) with no NaCl addition to 27.2 and 18.3 g/(mmol·h) respectively with addition of 1.71 and 8.55 mmol/L NaCl. Pham *et al.* [57] observed similar results when using SDS modi-

fied laterite to adsorb Copper (II) ion. They recorded increase in Cu^{2+} uptake from 150 to 185 mg/g as the ionic strength increased from 1 to 10 mmol/L. But further increase to 50 mmol/L NaCl caused reduction of uptake to 110 mg/g. These results also suggest that electrostatic and non-electrostatic (hydrophobic) attraction mechanisms are occurring during adsorption of inorganic contaminants by surfactant modified activated carbon.

3.1.7. Competing Ions

Industrial effluents hardly contain single inorganic ion. The co-ions will compete with the targeted ions for binding sites if they have preference for the same sites [58]. Chen *et al.* [25] added a varied (0.049 - 159.2 mg/L) of perchlorate, nitrate, sulphate or phosphate ions to a fixed bromate concentration (0.1 mg/L) to study its effect on the specific bromate uptake by CTAC modified activated carbon. The competing co-ions' inhibitory effect is insignificant at 10:1 co-ions to bromate molar ratio. This could be due to abundant active binding site at such low concentration. However, perchlorate and nitrate's inhibition became significant at 100:1 co-ions to bromate molar ratio while sulphate and phosphate's inhibition became significant at 1000:1 co-ions to bromate molar ratio. At the same co-ions to bromate molar ratio, competition followed decreasing order of $ClO_4^- > NO_3^- > SO_4^{2-} > PO_4^{3-}$. This order suggests that competition decreases as valence electrons increase. Other researcher observed similar results [59].

Mazarji *et al.* [27] also studied the effect of adding each of phosphate, carbonate, sulphate and chloride on the specific nitrate uptake by NaOH-CTAB modified activated carbon. The co-ions concentrations were varied from 20 to 160 mg/L while nitrate was fixed at 40 mg/L. Addition of each of the co-ions significantly reduced the specific nitrate uptake. Competition followed a decreasing order of $SO_4^{2-} > Cl^- > PO_4^{3-} > CO_3^{2-}$. The least effect of phosphate and carbonate was attributed to formation of H_2CO_3 and $H_2PO_4^-$ species which have less degree of competing with nitrate for active binding sites.

3.2. Surfactant Properties

Type of surfactant and surfactant concentration also contribute to the overall effectiveness of the modified activated carbons for adsorption of cations or anions from aqueous solution.

3.2.1. Type of Surfactant

Surfactant can be broadly classified into anionic, cationic and non-ionic. The targeted ion determines the type of surfactant required for modifying the activated carbon. This is because investigation into the mechanism of adsorption of ions by a surfactant modified activated carbon suggests that ion exchange is usually the main mechanism [21] [22] while other mechanism such electrostatic attraction, surface complexation and physical adsorption do complete it [23] [25]. Hence, if anion is the targeted contaminant to be removed from the aqueous solution, proper cationic surfactant is required for the modification of the activated

carbon [17] [21] [22] [27] [28] [29]. In contrast, if cation is the targeted contaminant, then proper anionic surfactant should be selected for the modification [23] [24] [26]. The flexibility in anchoring of surfactant onto the surface of activated carbon makes it one of the appealing surface modification methods.

3.2.2. Surfactant Concentration

The surfactant concentration used for modification of activated carbon also contributes to its adsorption capacity. Chen *et al.* [25] varied CTAC concentration from 0.2 to 8 mmol/L to obtain the proper surfactant concentration that maximise the uptake capacity of the modified activated carbon. The specific bromate uptake peaked at 2 mmol/L, equivalent to 1.26*critical micelle concentration of CTAC, below which the specific uptake steadily reduced and above which the specific uptake equally reduced.

Similarly, Kakavandi *et al.* [26] varied the SDS concentration from 0.5 to 5*CMC in order to optimise the specific Co (II) uptake by SDS modified activated carbon. The Co (II) removed peaked at 1.5*CMC of SDS, below and above which the specific uptake reduced steadily reaching the least value, 0% at 5*CMC. Of note is that at 6 h (optimised time) the specific uptake of the modified activated carbon for all concentration except 5*CMC were greater than that produced by virgin activated carbon.

Adsorption capacity of cationic or anionic surfactant modified activated carbon increase as surfactant concentration increases due to enhancement in their net surface positive or negative charge respectively. However, net surface charge of cationic surfactant modified activated carbons did not increase significantly beyond their CMC [22] while the surface area reduce [22] [24] [27] [28] due to surfactant blockage of micropores [24] [27]. This explains the reduction in specific ion uptake observed by Chen *et al.* [25] and Kakavandi *et al.* [26] with excessive increase in surfactant concentration above their CMC.

In addition, reduction of the micro-pore volume above CMC has high tendency of masking the active binding sites originally present on the virgin activated carbon thereby reducing their contribution to physical adsorption, surface complexation and electrostatic interaction to the main ion exchange. Few researchers fixed surfactant concentration below CMC [17] [27] or above CMC [21] during adsorption experiments. Such approach may prevent optimising the capacity of the modified activated carbons.

3.3. Activated Carbon Pre-Treatment

Alkali (NaOH) and acid (HNO_3) are the common reagents for treating activated carbon before surfactant modification to enhance their adsorption capacity.

3.3.1. Alkaline Pre-Treatment

Mazarji *et al.* [27] observed that treatment of activated carbon with NaOH at 75˚C for 7 h prior to CTAB surfactant modification enhances its adsorption for nitrate. They obtained percentage nitrate removed as NaOH-CTAB modified ac-

tivated carbon, 80% > NaOH treated activated carbon, 16% > virgin activated carbon, 8%. The observed enhancement was attributed to the increase in the specific surface area and micro pore volume caused by NaOH treatment. More micro pores allowed anchoring of more CTAB thereby increasing the net positive surface charge [60]. Increase in micro pores could increase nitrate uptake via hydrophobic interaction such as physical adsorption, surface complexation and non-electrostatic interaction [61]. NaOH pre-treatment improves removal/solubility of most organic components attached to virgin activated carbon into water by weakening their attractive van der Waals forces [24].

3.3.2. Acid Pre-Treatment

Sun *et al.* [24] treated activated carbon with HNO_3 before modification with sodium dodecyl benzene sulfonate (SDBS) to optimise its Cd (II) adsorption. HNO_3 concentration was varied from 0.5 - 4 mol/L, temperature, 60˚C - 100˚C, and SDBS, 5000 - 40,000 mg/L. The specific Cd (II) uptake by the HNO_3-SDBS modified activated carbon peaked at 3.29 mol/L HNO_3, 76˚C and 30, 700 mg/L SDBS. They observed that interaction of HNO_3 and surfactant concentration produced most significant effect on the maximum Cd (II) uptake capacity. The specific Cd (II) uptake capacity order obtained are HNO_3-SDBS modified activated carbon, 44.2 mg/g > SDBS modified activated carbon, 26.60 mg/g > HNO_3 modified activated carbon, 22.78 mg/g > virgin activated carbon, 6.78 mg/g. Of note is that the developed surface area, functional groups, and more net negative surface charge responsible for the higher adsorption capacity show by the HNO3-SDBS modified activated carbon.

4. Leaching of Surfactant Modified Carbon

Stability or leaching of surfactant modified activated carbon in aqueous solution should be considered during selection. This is important to ensure effluent quality and minimise secondary contaminants via surfactant desorption. Mazarji *et al.* [27] reported that CTAC did not leach in the lifetime of NaOH-CTAC modified activated carbon used. Tang *et al.* [21] also reported that CTAC modified activated carbon show good stability in water having 1.83% and 1.98% of the total CTAC loaded onto the activated carbon respectively leached in 2 and 32 days leaching test.

In contrast, Parette *et al.* [62] observed that 0.6% - 21% of the total amount of dicocodimethyl ammonium chloride, tallowtrimethyl ammonium chloride, cetyltrimethyl ammonium chloride leached out of the tailored carbon bed. However, virgin activated carbon polishing bed used to chase the tailored bed significantly reduced the leached surfactant below detection limits.

5. Regeneration

Regeneration of spent (saturated) modified activated carbons will minimise disposal. It will also make the process more environmental friendly, preserve our resources and more cost effective. Findings show that surfactant modified acti-

vated carbon can be regenerated. Cho *et al.* [29] desorbed nitrate and Cr (VI) ions from a saturated cationic (polymer) modified activated carbon using 0.05M NaOH (equivalent to pH 12.7). The modified reagent is cationic quaternary ammonium-containing polymer, [3-(methacryloylamino)propyl]-trimethylammonium chloride (CPMG) having similar property as cationic surfactant.

The specific nitrate uptake by the CPMG for the three consecutive adsorption/desorption cycles reduced from 21.4mg/g (for the fresh CPMG-activated carbon) to 19.4, 15.9, and 14.9 mg/g respectively. The regeneration efficiencies were 90.7%, 82%, and 93.7% respectively. The specific Cr (VI) uptake by the CPMG reduced from 59 mg/g (for the fresh CPMG-activated carbon) to 51.8, 49.3 and 45.5 mg/g respectively. The regeneration efficiencies were 87.8%, 95.2% and 92.3% respectively. At the 0.05 M NaOH (equivalent to pH 12.7) the net surface charge on the CPMG-activated carbon will be negative which will enhance desorption of the adsorbed negatively charges nitrate and Cr (VI) ions.

Tang *et al.* [21] used 1M HCl instead of NaOH to desorb perchlorate adsorbed to CTAC modified activated carbon. The specific perchlorate uptake of the fresh CTAC modified activated carbon was 24.06 mg/g. This value reduced to 23.07, 21.01, 19.12 and 18.99 mg/g respectively after four consecutive adsorption/regeneration cycles. The regeneration efficiencies were 95.88%, 91.46%, 90.62% and 99.32% respectively. Of note is that they obtained pHpzc for this CTAC modified activated carbon as 4.8 and the equivalent pH of 1M HCl used regeneration is pH 0, indicating highly acidic. The net surface charge of this adsorbent will be highly positive at this highly acid pH which ordinarily should enhance adsorption of the negatively charged perchlorate ion. The probable reason for the desorption observed could be due to protonation of perchlorate which will increase the repulsion between the adsorption perchlorate ions and the positively charged surface.

6. Conclusions

Surfactant concentration used for modification of activated carbon contributes to its specific contaminant uptake. The modified activated carbon usually shows maximum contaminant uptake around its critical micelle concentration.

Well-developed micro pores are required to allow anchoring of enough surfactant for high net surface charge and to minimise reduction in the specific surface area/micro pores volume after surfactant modification. Hot NaOH or HNO_3 treatment prior to surfactant modification has been shown to minimise surface area reduction and/or increase net surface charge of the modified activated carbons.

Solution pH is one of the key environmental parameters affecting adsorption capacity of the modified activated carbons and its variation can be used for regenerating the spent (saturated) modified activated carbon. Adsorption capacity of cationic modified activated carbon for targeted anion increases with decrease

in pH below pH_{pzc} but decreases with increase in pH above pH_{pz}. Adsorption capacity of anionic modified activated carbon for targeted cation increases with increase in pH above pH_{pzc} but decreases with decrease in pH below pH_{pzc}.

Overall, surfactant modification is a simple but efficient method of enhancing adsorption capacity of activated carbons for removing anions or cations from aqueous solution. However, a handful publication is available on the regeneration of the spent (saturated) surfactant modified activated carbons. Hence, more research efforts should be directed towards proper reagents and the optimised conditions such as contact time, concentration, and temperature for regenerating such modified activated carbons.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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