Comparison of Cationic Surfactants for Activated Carbon Modification for Cr(VI) Removal

W.F. Chen[*], J.H. Zhang, W.Y. Wang and X.M. Zhang

School of Environment and Architecture, University of Shanghai for Science and Technology, Shanghai 200093, P.R. China

*Corresponding author: Tel./Fax: +86 21 55275979; E-mail: chenzjzj@gmail.com

The study investigated the effect of cationic surfactants [*e.g.*, cetyltrimethylammonium chloride (CTAC), myristyltrimethylammonium bromide (MTAB) and decyltrimethylammonium bromide (DTAB)] loading on activated carbon and application of these modified carbons for Cr(VI) removal from aqueous phase. Adsorption isotherm tests indicate that the surfactant modification method was effective in improving activated carbon's adsorption capacity. At best, CTAC-modified carbon was able to adsorb 64.10 mg Cr(VI)/g at pH 6 as compared to that of 5.53 mg/g for virgin GAC. Langmuir isotherm and pseudo-second-order kinetics models were found to describe well the Cr(VI) adsorption behaviour on activated carbon. Also, adsorption of Cr(VI) decreased slightly with the increase of pH from 2 to 8 while adsorption was highly dependent on pH at pH 8-11. In addition, surfactant's attachment to carbon surface was strong and less than 5 % of the surfactant desorbed during Cr(VI) adsorption.

Keywords: Activated carbon, Cationic surfactant, Cr(VI), Adsorption.

INTRODUCTION

Chromate ions present in water has been the focus of many studies due to its toxicity[1]. Short-term exposure to chromate at levels above the maximum contaminant level (MCL) could cause skin irritation or ulceration while long-term exposure would potentially damage liver, kidney circulatory and nerve tissues[2]. Technologies for chromate removal include coagulation/flocculation, chemical precipitation, ion exchange, electrodeposition, adsorption and membrane processes *etc*.[3,4]. This research focused on activated carbon adsorption, specifically, adsorption by activated carbon modified by cationic surfactants.

Surfactants have a wide range of uses in industries[5]. Cationic surfactants are surfactants whose active portion bears a positive charge[6]. Amine salts and quaternary ammonium salts are the most common type of cationic surfactants. Quaternary ammonium functional groups are also regularly seen in anion exchange media since quaternary ammonium based compounds have a high pKa, rendering the positive charge virtually independent of pH in natural waters[7,8].

The emphasis of this research was on the impact of quaternary alkylammonium surfactants on adsorption of Cr(VI) by activated carbon. Natural or commercially available materials such as zeolite, bentonite, clinoptilolite and activated carbon have often found to be ineffective in removal of Cr(VI) or other toxic heavy metals[9,10]. Recent research has therefore focused on surface modification of a variety of solids to improve their capacities for heavy metals especially Cr(VI). Cationic surfactant-modified zeolite, clay, clinoptilolite and activated carbon showed great improvement in the removal of negatively charged particles, natural organic matter, arsenic or perchlorate[11-13]. In their investigation of activated carbon modification with cationic surfactant, Parette and Cannon revealed that they were able to load about 0.56-0.82 meq surfactant/g onto carbon surface and the modification led to about 30 times enhancement in perchlorate removal[14].

Studies have shown that the hydrophobic surface of activated carbon provided ample sites for the hydrophobic tail of the cationic surfactant to attach[15]. At the same time, the hydrophilic head of the surfactant extended towards the aqueous phase and where the majority of the adsorption occurred through electrostatic interaction or ion exchange[16,17]. The permanent positive charges of the quaternary alkylammonium functional groups make them ideal for adsorption of anionic metals. Besides, surfactants will have access to the micropores of the activated carbon. Equally as important as the ability to fit into the micropores, these surfactant species have been shown to have the ability to form ion pairs with anions in electrospray-mass spectrometry[18].

The main objectives of this research were to explore the effect of a number of cationic surfactants on the characteristics of activated carbon and ultimately the effect on adsorption of Cr(VI). The influence of initial surfactant concentration, surfactant loading level and solution pH were also investigated.

EXPERIMENTAL

Chromate solution was prepared from K_2CrO_4 (reagent grade, Alfa Aesar, China). A lignite-based granular activated carbon from Huayuan material Co. Ltd (China) was used as the virgin carbon. Organic cationic surfactant employed were decyltrimethylammonium bromide (DTAB), myristyltrimethylammonium bromide (MTAB) and cetyltrimethylammonium chloride (CTAC). They were all from Adamas Chemicals, China. The structure, molecular weight and critical micelle concentration (CMC) of these surfactants are shown in Table-1.

Cationic surfactant modification: 0.1 g of activated carbon was added to 50 mL of cationic surfactant solution with an array of initial concentrations ranging from 0.1-4.0 times of the critical micelle concentration (CMC) of the surfactant. The mixture was put on a shaker at 20 °C for 24 h. After that, carbon was separated and washed thoroughly with deionized-distilled water. Original solution and rinsing water were collected and analyzed for cationic surfactant. The amount of cationic surfactant loaded onto activated carbon was calculated from the difference between initial amount and what remains in aqueous phase. Cationic surfactant-modified activated carbons were named based on the type and initial concentration (represented in units of critical micelle concentration) of the surfactant. For instance, AC-CTAC-2 is a carbon modified by CTAC of 2 times the critical micelle concentration of CTAC. Non-modified activated carbon was named as activated carbon.

Adsorption isotherm: Adsorption isotherm tests were conducted using the bottle-point method. Deionized-distilled water (100 mL) that had been spiked with 20 mg/L as Cr of chromate was added to glass bottles containing 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1 or 2 g of carbon. The bottles were sealed and put on a shaker for 24 h at 20 °C. After that, carbon was separated and the aqueous phase chromate was monitored. pH of solutions were kept constant at 6.

Effect of pH: To determine the effect of pH, 0.1 g of activated carbon was added to glass bottles containing 100 mL of chromate (20 mg/L as Cr) solutions. The bottles were sealed and put on a shaker at room temperature (20 °C) for 24 h. Activated carbon was then filtered and filtrate was analyzed for both chromium and surfactant. pHs were adjusted to 2 to 11. 0.1 mol/L of NaOH and HCl solutions were used to adjust pH when needed.

Adsorption kinetics: In kinetics tests, 0.1 g of carbon was added to 10 syringes that each contained 100 mL of deionized-distilled spiked to 20 mg/L of Cr(VI) at pH 6. The syringes were mixed on an end-over-end shaker at room temperature. One syringe was taken off the shaker at 0.5, 1, 2, 3, 4, 6, 8, 10, 12 and 24 h and the mixture filtered through 0.45 μm filter paper.

Characterization of activated carbons: BET surface area and pore volume were determined from N_2 adsorption *via* ASAP 2010 systems (Micromeritics Instrument Corp., US). pHpzc of the activated carbons were analyzed by a one-point reverse mass titration method recommended by Noh and Schwarz[19]. One gram of sample was added to 10 mL of deionized water and the pH of the mixture (after 24 h equilibration) was taken as the equilibrium pH. The equilibrium pH is equivalent to the pHpzc. Scanning electron microscopy (SEM) (Quanta FEG 450) was used to observe the surface structure before and after modification.

Chemical analysis: Total chromium analysis was conducted *via* a Shimadzu Atomic Absorption Spectrophotometer with graphite furnace. A two-phase titration method with tetrabromophenolphthalein ethyl ester as indicator was employed to determine the concentration of cationic surfactant in solutions[20].

RESULTS AND DISCUSSION

Activated carbon modification by cationic surfactant: Fig. 1 is the loading of cationic surfactants at various initial surfactant concentrations. Concentration was represented in units of critical micelle concentration. As shown in Fig. 1, DTAB loading increased with the increase of initial concentration at the beginning and reached 0.6 mmol/g activated carbon at 1 critical micelle concentration (16 mmol/L). Further increase of surfactant concentration to 4 critical micelle concentration (64 mmol/L) showed little increase. At 4 critical micelle concentration, surfactant loading was 0.65 mmol/g. Critical micelle concentration is the concentration of an amphiphilic component in solution at which aggregates (micelles, round rods *etc.*) start to form in the solution[21]. It is believed that hydrophobic interactions or micelle aggregates determined the extent of surfactant loading on solid surfaces[22]. When concentration of surfactant was lower than critical micelle concentration (CMC), surfactant molecules existed mainly as monomers and were

TABLE-1
CHARACTERISTICS OF CATIONIC SURFACTANTS

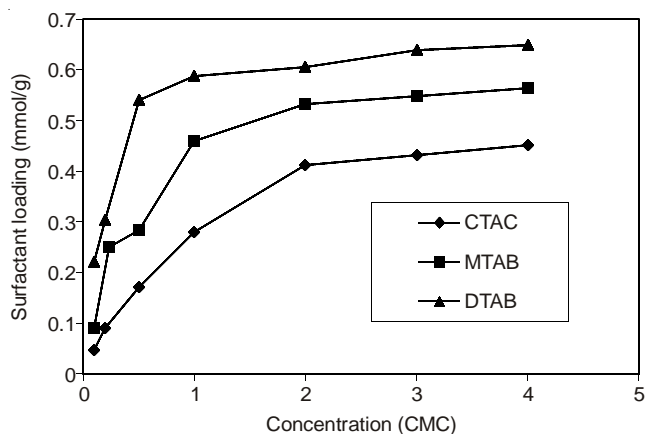| Surfactant	Structure	m.w.	CMC (mmol/L)
Cetyltrimethylammonium chloride (CTAC)	$CH_3(CH_2)_{14}CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}-CH_3 \quad Cl^-$	320	1.25
Myristyltrimethylammonium bromide (MTAB)	$CH_3(CH_2)_{12}CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}-CH_3 \quad Br^-$	336.4	3.4
Decyltrimethylammonium bromide (DTAB)	$CH_3(CH_2)_8 CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}-CH_3 \quad Br^-$	280.3	16.0

Fig. 1.   Cationic surfactant loading on activated carbon at different initial concentration

easily adsorbed onto activated carbon surface. As concentration approached critical micelle concentration, micelle formation was initiated. This aggregation accelerated as concentration increased. DTAB loading slowed down after 1 critical micelle concentration. The formation of micelle may affect the diffusion of surfactant to activated carbon surface.

For CTAC and MTAB, loading on activated carbon also started to level off after concentration reached above critical micelle concentration value. And the maximum loadings were around 0.45 and 0.56 mmol/g respectively.

Characterization of cationic surfactant-modified activated carbons: Fig. 2a and d is the SEM images of virgin activated carbon and some of the surfactant-modified activated carbons. Virgin activated carbon (Fig. 2a) showed well developed pore structure. At 1 critical micelle concentration of surfactant concentration, there was an obvious layer of cationic surfactant for both CTAC and MTAB (Fig. 2b and d). As shown in Fig. 2(d), MTAB aggregate had a round rod shape while CTAC showed spherical micelle aggregate (Fig. 2c). Fig. 2b is the image of 0.5 critical micelle concentration of CTAC-modified activated carbon. At 0.5 critical micelle concentration, there is no visible form of aggregate and only a thin layer of CTAC was observed. DTAB also showed spherical micelle

aggregate at carbon surface at concentration above critical micelle concentration (SEM images not shown here).

Also, from the SEM images, surfactant loading resulted in the blockage of some of the original pore structures. The blockage is much more obvious for AC-CTAC-1 than for AC-CTAC-0.5 (Fig. 2 b and c). This is confirmed by the decrease in surface area and pore volume.
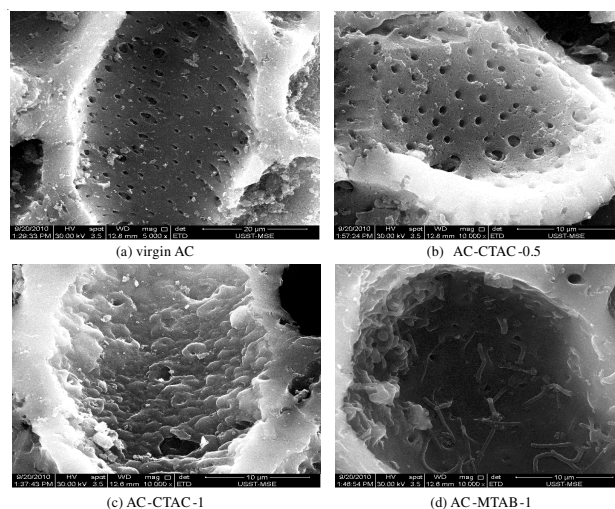

Fig. 2. SEM image of virgin and cationic surfactant-modified activated carbons

Table-2 lists the BET surface area, micropore and mesopore volumes of the virgin activated carbon and some of the surfactant-modified samples. For modified carbons, there are significant decreases both in surface area and pore volume with the increase of initial surfactant concentrations. For example, after 4 critical micelle concentration (5 mmol/L) of CTAC loading, carbon's surface area dropped from 710 to 236 m^2/g. And most of the pore volumes were lost. Micropore volume for AC-CTAC-4 is 0.09 mL/g as compared to that of 0.27 mL/g for virgin activated carbon.

pHpzc is the pH where carbon presents a net surface charge of zero and is directly related to surface charge distribution. Surface of carbon presents a net positive charge at pH < pHpzc and a net negative charge at pH > pHpzc[23]. pHpzc is 6.1 for virgin

TABLE-2
BET SURFACE AREA, PORE VOLUME AND pHpzc OF VIRGIN AND MODIFIED ACTIVATED CARBONS

Sample	BET surface area (m^2/g)	Micropore volume (< 20 Å) (mL/g)	Mesopore volume (20-500 Å) (mL/g)	pHpzc
Virgin AC	710	0.27	0.078	6.1
AC-CTAC-0.1	645	0.22	0.064	9.8
AC-CTAC-0.2	620	0.22	0.067	10.2
AC-CTAC-0.5	568	0.18	0.055	10.5
AC-CTAC-1	520	0.15	0.041	11.0
AC-CTAC-2	358	0.10	0.022	10.4
AC-CTAC-4	236	0.09	0.013	10.7
AC-MTAB-0.1	652	0.23	0.055	10.1
AC-MTAB-0.2	610	0.21	0.041	10.5
AC-MTAB-0.5	545	0.20	0.039	10.5
AC-MTAB-1	490	0.16	0.022	10.7
AC-MTAB-2	261	0.10	0.016	10.7
AC-DTAB-0.1	585	0.19	0.051	9.9
AC-DTAB-0.2	480	0.15	0.047	10.1
AC-DTAB-0.5	244	0.08	0.035	10.9
AC-DTAB-1	189	0.06	0.024	10.6
AC-DTAB-2	150	0.04	0.011	10.8

GAC. After surfactant modification, pHpzc values increased to around 9.8-11 (Table-2). This indicates that modified carbons are positively charged at pHs mostly encountered in natural waters and this can only be beneficial for anion adsorption.

Adsorption isotherm for Cr(VI): Batch adsorption isotherm tests were carried out to screen the surfactant-modified activated carbons. Solution pH was controlled at pH 6. Figs. 3-5 are adsorption isotherms for CTAC, MTAB and DTAB-modified carbons, respectively. Data were fitted to Freundlich and Langmuir models. Table-3 is the parameters for these adsorption models. Based on the correlation coefficient (R^2), Langmuir model was better in explaining the adsorption behaviour of Cr(VI) with R^2 between 0.91 and 0.99. This is in accordance with other studies on Cr(VI) removal by cationic surfactant-modified solid surface[24]. Langmuir model assumes monolayer adsorption. Studies have shown that Cr(VI) adsorption on cationic surfactant-modified surface most likely occurred through electrostatic interaction and this adsorption is site specific and demonstrated a monolayer formation[25,26].

Surfactant modification greatly improved carbon's adsorption capacity for Cr(VI). q_{max} for virgin activated carbon is
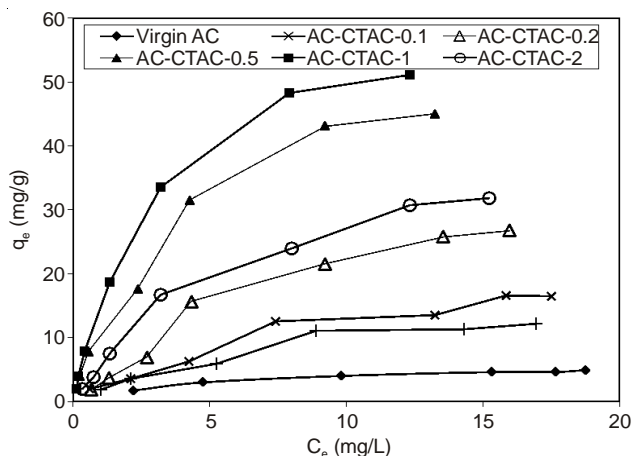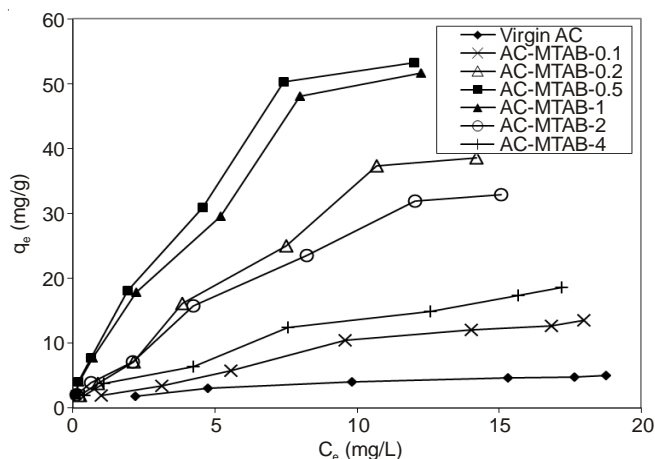

Fig. 4. Adsorption isotherm for virgin and MTAB-modified carbons
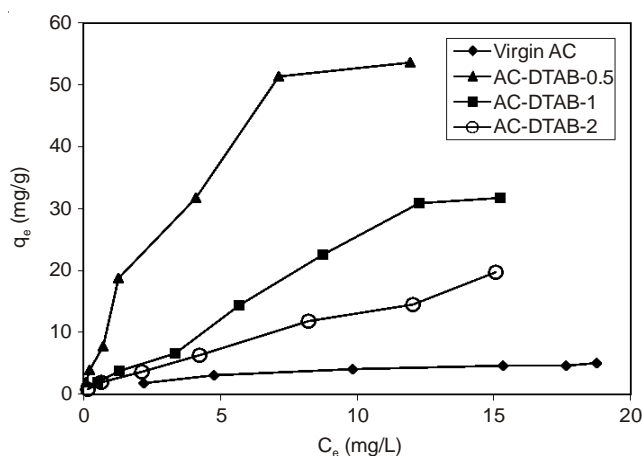

Fig. 5. Adsorption isotherm for virgin and DTAB-modified carbons

5.53 mg/g. After modification, AC-CTAC-1 showed the maximum adsorption capacity of 64.10 mg/g. With CTAC modification, adsorption capacity represented by q_{max} increased with the increase of initial surfactant concentration up to 1 critical micelle concentration (1.25 mmol/L). Further increasing the

Fig. 3. Adsorption isotherm for virgin and CTAC-modified carbons

TABLE-3
ISOTHERM PARAMETERS FOR Cr(VI) BY VIRGIN AND MODIFIED ACTIVATED CARBONS

Sample	Freundlich isotherm $q = K_f C^{1/n}$			Langmuir isotherm $q = \dfrac{q_{max} bCe}{1 + bCe}$		
	K_f (mg/g (mg/L)$^{-1/n}$)	$1/n$	R^2	q_{max} (mg/g)	b	R^2
Virgin AC	1.39	0.42	0.92	5.53	0.22	0.95
AC-CTAC-0.1	2.53	0.67	0.91	13.74	0.27	0.94
AC-CTAC-0.2	3.60	0.65	0.90	26.18	0.17	0.98
AC-CTAC-0.5	21.98	0.58	0.93	46.73	0.37	0.99
AC-CTAC-1	12.81	0.73	0.91	64.10	0.31	0.98
AC-CTAC-2	5.21	0.73	0.90	30.30	0.22	0.97
AC-CTAC-4	2.03	0.73	0.89	18.52	0.11	0.99
AC-MTAB-0.1	1.75	0.72	0.91	15.22	0.13	0.95
AC-MTAB-0.2	4.85	0.79	0.91	21.74	0.38	0.94
AC-MTAB-0.5	11.13	0.68	0.94	46.08	0.51	0.98
AC-MTAB-1	10.59	0.67	0.87	43.86	0.43	0.99
AC-MTAB-2	5.81	0.62	0.98	15.87	0.42	0.91
AC-MTAB-4	3.32	0.60	0.94	14.08	0.37	0.96
AC-DTAB-0.1	5.87	0.82	0.9	42.01	0.22	0.98
AC-DTAB-0.2	4.85	0.79	0.91	59.88	0.21	0.94
AC-DTAB-0.5	11.70	0.72	0.98	33.67	0.37	0.98
AC-DTAB-1	3.60	0.82	0.93	32.36	0.12	0.98
AC-DTAB-2	2.66	0.68	0.94	8.54	0.45	0.96

concentration to 2 and 4 critical micelle concentration actually caused decrease in q_{max} despite higher surfactant loading from AC-CTAC-2 and AC-CTAC-4. As shown in Fig. 1, there is steady increase in the amount of surfactant loaded as the increase of initial surfactant concentration. It appears that higher surfactant loading did not always result in higher Cr(VI) removal. This may be due to the distribution of surfactant that was loaded onto carbon surface. As obvious from surface area and pore volume (Table-2), surfactant loading clogged many of the activated carbon's pore structures. This blockage may obstruct diffusion of Cr(VI) to the adsorption sites and a portion of the loaded surfactant may not be accessible to Cr(VI). The results highlight that accessibility also plays a significant role in adsorption.

The same is with MTAB and DTAB. The highest adsorption capacities for MTAB and DTAB are with AC-MTAB-0.5 (46.08 mg/g) and AC-DTAB-0.2 (59.88 mg/g), respectively. Increase the initial surfactant concentration to beyond 0.5 critical micelle concentration for CTAB and 0.2 critical micelle concentration for DTAB saw decrease in their adsorption capacities.

Overall, AC-CTAC-1, AC-MTAB-0.5 and AC-DTAB-0.2 obtained the highest adsorption capacity in their respective category. As shown in Table-1, critical micelle concentrations for CTAC, MTAB and DTAB are 1.25, 3.4 and 16 mmol/L. Factoring in the actual critical micelle concentration values, the maximum adsorption occurred on activated carbons were those modified by 1.25 mmol/L CTAC or 1.6 mmol/L MTAB or 3.2 mmol/L DTAB. From Fig. 1, at these initial concentrations, the amount of surfactant loaded are 0.28, 0.28 and 0.30 mmol/g for CTAC, MTAB and DTAB, respectively. It appears that for this particular carbon, a loading of surfactant at around 0.3 mmol/g provided the best combination of availability and accessibility. If less than 0.3 mmol/g of surfactant was loaded, there may not be enough surfactant anion exchange sites for Cr(VI) while excessive surfactant loading could lead to blockage of pore structure thus site obstruction.

In addition, CTAC-modified activated carbon had the highest adsorption capacity among the three cationic surfactants. This is in accordance with the study of Li and Bowman[27]. Li and Bowman investigated the counter ion effects on the sorption of cationic surfactant and chromate. They stated that cationic surfactant with Cl⁻ as counter ion had greater adsorption for CrO_4^{2-} than those with Br⁻ even though the former demonstrated higher loading on carbon surface. They attributed the difference to the fact that hydrated Cl⁻ is larger than Br⁻ thus a weaker bond to the surfactant. In this study, AC-CTAC-1, AC-MTAB-0.5 and AC-DTAB-0.2 obtained similar surfactant loading, but CTAC had significantly higher q_{max} than MTAB and DTAB. The result here may be another piece of evidence that counter ion can be a factor in chromate ion adsorption for surfactant-modified activated carbon.

Effect of pH on Cr(VI) adsorption: Samples that demonstrated the best adsorption capacities for Cr(VI), that is, AC-CTAC-1, AC-MTAB-0.5 and AC-DTAB-0.2 were further studied for the effect of pH on Cr(VI) adsorption. Fig. 6 is the effect of pH on virgin activated carbon and three modified carbons. pH ranged from 2 to 11. In addition, stability of loaded surfactant is another concern with the modified carbons. Fig. 7
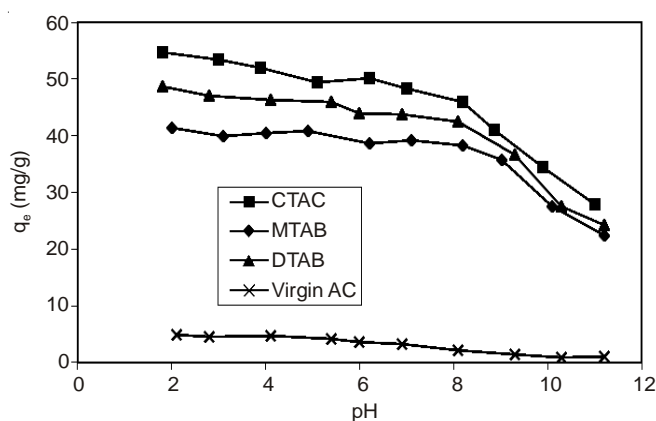

Fig. 6.   Effect of pH on Cr(VI) adsorption by virgin and modified activated carbons
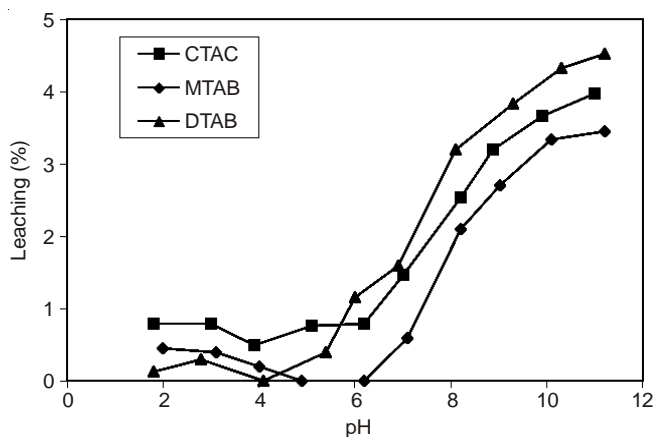

Fig. 7. Cationic surfactant desorption at different pHs

Fig. 7 is the percentage of surfactant that leached out of activated carbon at various pH.
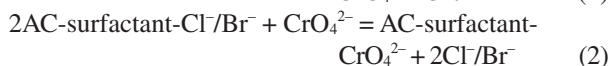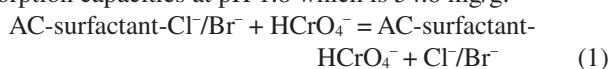
As shown in Fig. 6, Cr(VI) removal decreased steadily with the increase of pH for virgin activated carbon. Virgin activated carbon had a pHpzc of 6.1. This means that the net surface charge of virgin activated carbon shifts from positive to negative around pH 6.1. At pH < 6, negatively charged Cr(VI) in the forms of $HCrO_4^-$ or CrO_4^{2-} can be removed through electrostatic attraction on the carbon's positively charged sites. But with the increase of pH, carbon surface became increasingly negative. At pH > 6, the carbon surface became predominantly negative. Therefore, pH increase resulted in stronger electrostatic repulsion than attraction thus the decrease in removal.

All three modified carbons showed similar pattern at different pHs. The adsorption capacities was only slightly dependent on pH at pHs < 8. With pHpzc of 9.8-11.0, modified carbons are predominantly positively charged at low pHs. This may explain the very stable adsorption as pH increased from 2 to 8. However, a sharp drop was observed at pH > 8. This is mainly attributed to the speciation of Cr(VI) in aqueous phase. Anion exchange is supposedly the main mechanism of Cr(VI) adsorption as shown in eqn. 1 and 2. Though Cr(VI) exists mostly as anionic species over the entire pH range with H_2CrO_4 dominant only at pH < 1. At pH of 1.0-5.0, $HCrO_4^-$ is the predominant species[28]. At higher pH, the forms shift to CrO_4^{2-} and $Cr_2O_7^{2-}$. As pH increases from 2 to 7, $HCrO_4^-$ increases while H_2CrO_4

TABLE-4
KINETICS PARAMETERS FOR Cr(VI) BY VIRGIN AND MODIFIED ACTIVATED CARBONS

Sample	Pseudo-first order		Pseudo-second order	
	K_1 (h^{-1})	R^2	K_2 (g/mg h)	R^2
Virgin AC	0.42	0.70	0.57	0.89
AC-CTAC-1	0.21	0.56	0.33	0.92
AC-MTAB-0.5	0.25	0.67	0.28	0.97
AC-DTAB-0.2	0.24	0.64	0.31	0.94

decreases, negatively charged $HCrO_4^-$ is readily adsorbed through electrostatic interaction with positively charged surfactant on carbon surface. The adsorption mostly occurred as depicted in eqn. 1. As pH increases beyond 7, CrO_4^{2-} dominance increases and it would need 2 units of positive sites to adsorb one unit of CrO_4^{2-} as shown in eqn. 2. For instance, at pH 11, AC-CTAC-1 adsorbed 27 mg Cr/g which is about half of its adsorption capacities at pH 1.8 which is 54.8 mg/g.

$$AC\text{-}surfactant\text{-}Cl^-/Br^- + HCrO_4^- = AC\text{-}surfactant\text{-}$$
$$HCrO_4^- + Cl^-/Br^- \qquad (1)$$
$$2AC\text{-}surfactant\text{-}Cl^-/Br^- + CrO_4^{2-} = AC\text{-}surfactant\text{-}$$
$$CrO_4^{2-} + 2Cl^-/Br^- \qquad (2)$$

In addition, it turns out that surfactant attached strongly to carbon surface. As shown in Fig. 7, less than 5 % of the originally loaded surfactant leached out at pH = 11. Surfactant concentration in solution was less than 0.01 mmol/L at all pHs. There is slight increase in surfactant desorption with the increase of pH at pH > 6. This behaviour may be explored further as means of carbon regeneration.

Adsorption kinetics: Adsorption kinetics tests were carried out to obtain the Cr(VI) adsorption rates on modified carbons. Pseudo-first-order and pseudo-second-order models were employed to describe the process of Cr(VI) adsorption.

Pseudo-first-order kinetic model: $\log(q_e\text{-}q_t) = \log q_e - \dfrac{K_1}{2.303} t$

Pseudo-second-order kinetic model: $\dfrac{t}{q_t} = \dfrac{1}{K_2 q_e^2} + \dfrac{1}{q_e} t$

where q_e and q_t are Cr(VI) adsorption at equilibrium and time t, K_1 and K_2 are adsorption rate constants.

Fig. 8 is the kinetics test for virgin activated carbon, AC-CTAC-1, AC-MTAB-0.5 and AC-DTAB-0.2. Table-4 summarizes the kinetic parameters from fitting the models. The adsorption data fit the psdudo-second-order model the best. In addition, modification by surfactant had a great effect on the rate of Cr(VI) adsorption. Adsorption rate is 0.57 g/mg h for virgin AC while those of modified carbons ranged from 0.28 to 0.33 g/mg h. This is in accordance with the observation that surfactant loading may cause obstructing of Cr(VI) diffusion to the specific adsorption sites thus a slower rate of adsorption.

Conclusion

Cationic surfactant modification was proven to be effectively in enhancing adsorption of Cr(VI) by activated carbon. Specifically, virgin activated carbon could only adsorb about 5.53 mg Cr(VI)/g activated carbon. In contrast, at best, the CTAC-modified carbon achieved an adsorption capacity of 64.10 mg Cr/g by adsorption isotherm tests. Cationic surfactants such as MTAB and DTAB were also very effective. Adsorption
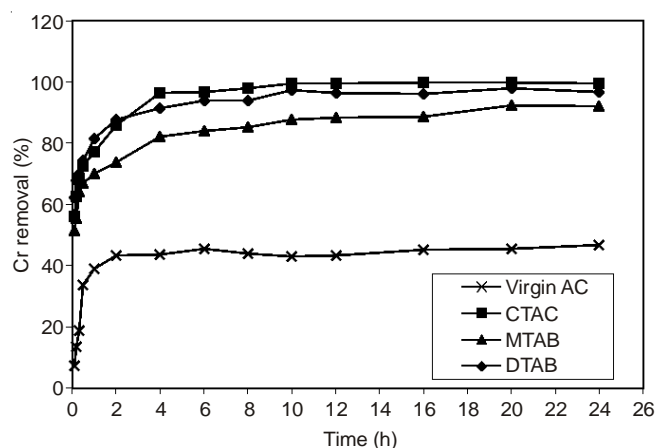

Fig. 8. Adsorption kinetics of virgin and modified activated carbons

capacities increased by 8-10 times after modification by these two surfactants. In addition, besides the amount of surfactant loading, it appears that the accessibility of these loaded surfactants to Cr(VI) played another important role. For the carbon studied here, around 0.3 mmol surfactant/g loading is the optimum. Higher loading resulted in the obstruction of Cr(VI) diffusion and actually less adsorption. The presence of surfactant decreased the Cr(VI) adsorption rate though adsorption was still fast with 80 % of the Cr(VI) adsorbed in the first 3 h of contact. In addition, Cr(VI) adsorption was dependent on pH only at pH > 8. At high pHs, modified carbon showed sharp drop in Cr(VI) adsorption with the increase of pH. Overall, Cr(VI) was removed through an anion exchange process with the loaded surfactant. The study also revealed that the loaded surfactants were quite stable on activated carbon surface and only desorbed at extreme high pH.

REFERENCES

1. M. Costa, *Toxicol. Appl. Pharmacol.*, **188**, 1 (2003).
2. J. Su, H.G. Huang, X.Y. Jin, X.Q. Lu and Z.L. Chen, *J. Hazard. Mater.*, **185**, 63 (2011).
3. T. Kameda, E. Kondo and T. Yoshioka, *Sep. Purif. Technol.*, **122**, 12 (2014).
4. S. Chakraborty, J. Dasgupta, U. Farooq, J. Sikder, E. Drioli and S. Curcio, *J. Membr. Sci.*, **456**, 139 (2014).
5. A.L. Ahmad and S.W. Puasa, *Chem. Eng. J.*, **132**, 257 (2007).
6. N. Haq, M. Usman, A. Mansha, M.A. Rashid, M. Munir and U.A. Rana, *J. Mol. Liq.*, **196**, 264 (2014).
7. N. Azum, M.A. Rub and A.M. Asiri, *J. Mol. Liq.*, **196**, 14 (2014).

8. A. Jayalakshmi, S. Rajesh, S. Senthilkumar and D. Mohan, *Sep. Purif. Technol.*, **90**, 120 (2012).

9. Y. Sun, Q. Yue, Y. Mao, B. Gao, Y. Gao and L. Huang, *J. Hazard. Mater.*, **265**, 191 (2014).

10. A.M. Yusof and N.A.N.N. Malek, *J. Hazard. Mater.*, **162**, 1019 (2009).

11. S.Y. Lin, W.F. Chen, M.T. Cheng and Q. Li, *Colloids Surf. A*, **434**, 236 (2013).

12. H.D. Choi, J.M. Cho, K. Baek, J.S. Yang and J.Y. Lee, *J. Hazard. Mater.*, **161**, 1565 (2009).

13. E. Ergican and H. Gecol, *J. Membr. Sci.*, **325**, 69 (2008).

14. R. Parette and F.S. Cannon, *Water Res.*, **39**, 4020 (2005).

15. C.C. Berton-Carabin, J.N. Coupland, C. Qian, D.J. McClements and R.J. Elias, *Colloids Surf. A*, **412**, 135 (2012).

16. Syafalni, R. Abdullah and P.S. Ushaa Nair, *World Appl. Sci. J.*, **27**, 614 (2013).

17. M. Soria-Sanchez, A. Maroto-Valiente, A. Guerrero-Ruiz and D.M. Nevskaia, *J. Colloid Interf. Sci.*, **343**, 194 (2010).

18. A. Wypych, K. Szpotkowski, S. Jurga, L. Domka and M. Kozak, *Colloids Surf. B*, **108**, 212 (2013).

19. J.S. Noh and J.A. Schwarz, *Carbon*, **28**, 675 (1990).

20. M. Tsubouchi, H. Mitsushio and N. Yamasaki, *Anal. Chem.*, **53**, 1957 (1981).

21. I.A. Khan, A.J. Khanam, M.S. Sheikh and Kabir-ud-Din, *J. Colloid Interf. Sci.*, **359**, 467 (2011).

22. L. Chen and H. Xie, *Thermochim. Acta*, **506**, 62 (2010).

23. A. Kawashima, M. Katayama, N. Matsumoto and K. Honda, *Chemosphere*, **83**, 823 (2011).

24. A. Benhammou, A. Yaacoubi, L. Nibou and B. Tanouti, *J. Hazard. Mater.*, **140**, 104 (2007).

25. M. Nadeem, M. Shabbir, M.A. Abdullah, S.S. Shah and G. McKay, *Chem. Eng. J.*, **148**, 365 (2009).

26. M.C. Brum, J.L. Capitaneo and J.F. Oliveira, *Miner. Eng.*, **23**, 270 (2010).

27. Z. Li and R.S. Bowman, *Environ. Sci. Technol.*, **31**, 2407 (1997).

28. Y. Zeng, H. Woo, G. Lee and J. Park, *Desalination*, **257**, 102 (2010).