



## Study on Adsorption Selectivity of Inorganic Oxyanions' by Granular Activated Carbon Modified with Cationic Surfactant

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A granular activated carbon (GAC) modified by cationic surfactant cetyltrimethylammonium chloride (GAC-CTAC) was investigated for its adsorption of oxyanions (perchlorate, bromate, arsenate, nitrate, sulfate and phosphate). GAC-CTAC showed adsorption capacities 4-7 times those of virgin granular activated carbon. The free energies of adsorption by virgin granular activated carbon and GAC-CTAC showed that cationic surfactant modification changed the interaction between adsorbent and adsorbate. Ion exchange played a major role in adsorption with GAC-CTAC. In addition, GAC-CTAC showed different levels of selectivity towards oxyanions. Results reveal that GAC-CTAC was more selective towards perchlorate, bromate and nitrate than arsenate, sulfate and phosphate. Moreover, selectivity was highly dependent upon oxyanion's free energies of hydration and adsorption.

**Keywords:** Oxyanion, Granular activated carbon, Cationic surfactant, Selectivity, Column tests.

### INTRODUCTION

Increased industrial and agricultural activities have raised public concerns about quality of drinking water sources worldwide since large numbers of toxic pollutants, inorganic anions, metal ions, synthetic organic chemicals, were generated every year. Inorganic oxyanions such as perchlorate, bromate, arsenate, nitrate, sulfate and phosphate exist in various concentrations depending upon the pollution levels of water bodies. Origins of perchlorate and bromate are mostly anthropogenic. Perchlorate ( $\text{ClO}_4^-$ ) is a strong oxidizer that has found uses as propellant in rockets, missiles and fireworks. Most of the perchlorate contamination in the environment is connected to sites that have manufactured or used perchlorate<sup>1</sup>. In water treatment processes, bromate is formed during ozonation, hypochlorination or chloramination of water containing bromide<sup>2</sup>. Arsenate is the predominant and stable inorganic arsenic form in oxygen-rich aerobic environments. Most reported arsenic problems are found in groundwater supply systems and are caused by natural processes such as mineral weathering and dissolution resulting from a change in the geo-chemical environment to a reductive condition<sup>3,4</sup>. Arsenic contamination is also caused by human activities like mining wastes, petroleum refining, sewage sludge, agricultural chemicals, ceramic manufacturing industries and coal fly ash<sup>5,6</sup>. Nitrate, sulfate and phosphate are commonly present both in surface and

ground water. They are possibly the most widespread contaminants in the world. Nitrate and phosphate at high concentration impose a serious threat to drinking water supplies and promoting eutrophication. Sulfate is one of the main contributors to so-called water "mineralization", thereby increasing the conductivity and corrosion potential of receptor bodies<sup>7</sup>.

Regulations on these anions become more stringent with the increase in the understanding of their effects to environment. Technologies need to be developed to meet the new demands. Adsorption is one of the many technologies employed to remove oxyanions from water. With its advantages in cost, availability and structural strength, activated carbon is commonly acknowledged as effective to remove an array of organics and inorganics.

Cationic surfactant modification of granular activated carbon (GAC)<sup>8,9</sup>, powdered activated carbon (PAC)<sup>10</sup>, zeolite<sup>11</sup> and erionite<sup>12</sup> showed various degrees of improvements for oxyanions adsorption. Adsorption of anion by surfactant-modified adsorbents was mostly attributed to ion exchange, electrostatic attraction or surface complexation. Parette and Cannon<sup>13</sup> believed that removal of perchlorate by a cetyltrimethylammonium chloride (CTAC)-modified GAC was most likely due to ion exchange. Xu *et al.*<sup>14</sup> however suggested that ion exchange only accounted for part of the perchlorate removal. Electrostatic attraction also played a role.

One factor that could seriously affect adsorption capacity is the presence of other adsorbates<sup>15,16</sup>. Co-existing adsorbates were shown to compete for the same adsorption sites<sup>17</sup>. In oxyanion removal, competition with other anions was found to be particularly noteworthy. Chitrakar *et al.*<sup>18</sup> employed cetylpyridinium chloride (CPC)-modified organo-montmorillonite (CPC-mont) for removal of bromate. The presence of nitrate decreased the amounts of bromate adsorbed by up to 99%. Furthermore, CPC-mont's selectivity was in the order of nitrate > bromide > bromate > sulfate > phosphate. Mahmudov and Huang<sup>19</sup> investigated selective adsorption of oxyanions on activated carbon F400 and concluded that perchlorate and nitrate prefer the same adsorption sites and adsorption of perchlorate decreased when nitrate was present and *vice versa*.

The objectives of this study were to: (1) study the adsorption of oxyanions by a cationic surfactant-modified GAC and explore the mechanism of adsorption; (2) investigate the selectivity of this modified GAC towards different oxyanions.

## EXPERIMENTAL

Granular activated carbon (lignite-based) was procured from Huayuan material Co. Ltd (China) and had a surface area of 710 m<sup>2</sup>/g and a total pore volume of 0.35 mL/g. Before use, it was ground to US mesh size 200 × 400 (37 × 74 μm). Cationic surfactant cetyltrimethylammonium chloride (CTAC) was from Adamas Chemicals (China). Sodium salts of bromate, perchlorate, arsenate, nitrate, sulfate, phosphate and chloride were all purchased from China Chemicals Inc.

**Preparation of cationic surfactant-modified granular activated carbon:** 0.2 g of granular activated carbon was added to 250 mL Pyrex glass bottle which contained 200 mL of 2 mmol/L of CTAC solution made from deionized water. The mixture was put on a shaker at 20 °C for 24 h. After that, activated carbon was separated by filtration (0.2 μm filter paper) and washed thoroughly with deionized water till no CTAC was detected in effluent. The amount of CTAC loaded was measured to be 0.18 mmol/g. Modified activated carbon was named as GAC-CTAC. Non-modified GAC was named as virgin GAC.

**Adsorption isotherms:** Adsorption isotherm tests were conducted at room temperature (20 °C). 0.05, 0.1, 0.2, 0.5, 1, 2 and 5 g of activated carbon, respectively, were added to 100 mL of solution which contained 20 mg/L of oxyanion. The mixture was allowed to equilibrate for 24 h. Adsorption isotherm data were fitted to Langmuir and Freundlich model as shown in equations (1) and (2), where  $C_e$  is the concentration at equilibrium,  $q_e$  is the amount adsorbed at equilibrium.  $q_{\max}$ ,  $b$ ,  $K_F$  and  $1/n$  are constants.  $q_{\max}$  is the maximum adsorption capacity,  $b$  is related to the free energy of adsorption.  $K_F$  and  $1/n$  are related to the capacity and strength of adsorption respectively.

$$\text{Langmuir adsorption: } q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (1)$$

$$\text{Freundlich adsorption: } q_e = K_F C_e^{1/n} \quad (2)$$

During isotherm tests, after equilibrium was reached, concentration of chloride in the solutions were measured and compared with the amount of oxyanions adsorbed.

**Distribution coefficient:** 0.2 g of activated carbon was added to 100 mL of solution which contained 0.01, 0.1, 1 or 2 mmol/L of 6 anions (perchlorate, bromate, nitrate, arsenate, sulfate and phosphate). The mixture was equilibrated for 24 h and filtered. Filtrate was analyzed for anions. Distribution coefficient  $K_d$  was calculated as below:

$$K_d \text{ (L/mg)} = \frac{\text{anion adsorbed (mg/g)}}{\text{anion remained (mg/L)}} \quad (3)$$

All tests were conducted in triplicate and data presented was the average.

**Analytical methods:** Concentrations of bromate, perchlorate, nitrate, sulfate and phosphate were analyzed by a Thermo Scientific ICS-2100 ion chromatography system. Arsenic analysis was conducted *via* a Shimadzu Atomic Absorption Spectrophotometer (AA-6800F) with graphite furnace.

## RESULTS AND DISCUSSION

**Adsorption isotherms:** Adsorption isotherms of individual oxyanion were carried out first to study the effect of cationic surfactant modification. Figs. 1 and 2 are the adsorption isotherms of GAC-CTAC and virgin GAC. Tables 1 and 2 list the adsorption parameters after data were fitted to Langmuir and Freundlich adsorption equations. Correlation coefficients ( $R^2$ ) showed a much better fit with Langmuir than Freundlich indicating that oxyanion adsorption is more likely single layer and can occur only at a fixed number of localized sites. Adsorption of oxyanions improved after CTAC modification. GAC-CTAC showed the highest capacity for perchlorate and bromate with maximum adsorption of 29.76 and 30.30 mg/g, respectively.

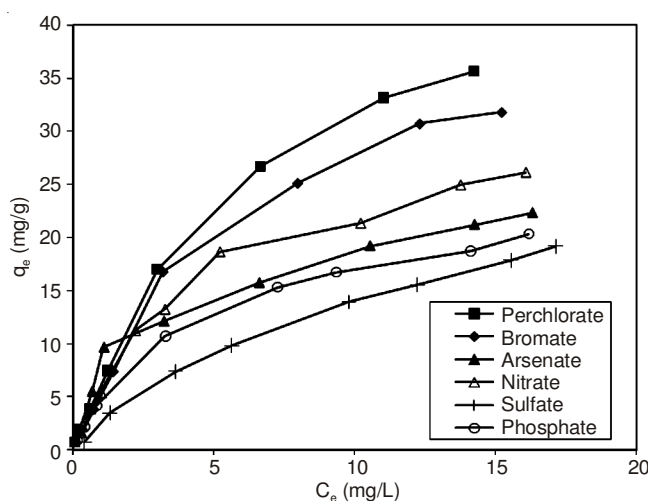


Fig. 1. Adsorption isotherms of oxyanions for GAC-CTAC

Cetyltrimethylammonium chloride contained a quaternary ammonium head group. This functional group is commonly seen in ion exchange resin. Gu *et al.*<sup>20</sup> reported that a "bifunctional resin", consisting of quaternary ammonium groups with C<sub>6</sub> and C<sub>2</sub> alkyl groups, had a high selectivity for perchlorate. It was hypothesized that an ion exchange process shown as follows with GAC-CTAC may be the main mechanism for oxyanion.

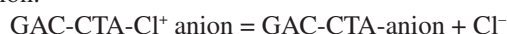


TABLE-1  
LANGMUIR PARAMETERS OF ADSORPTION FOR GAC-CTAC AND VIRGIN GAC

Oxyanion	Langmuir					
	GAC-CTAC			Virgin GAC		
	$q_{\max}$ (mg/g)	$b$ (L/mg)	$R^2$	$q_{\max}$ (mg/g)	$b$ (L/mg)	$R^2$
Perchlorate	29.76	0.31	0.96	4.78	0.12	0.98
Bromate	30.30	0.28	0.93	4.12	0.11	0.96
Arsenate	21.85	0.34	0.96	4.31	0.14	0.95
Nitrate	27.93	0.13	0.95	2.34	0.11	0.94
Sulfate	15.08	0.54	0.98	3.94	0.09	0.99
Phosphate	24.21	0.21	0.97	3.67	0.09	0.98

TABLE-2  
FREUNDLICH PARAMETERS OF ADSORPTION FOR GAC-CTAC AND VIRGIN GAC

Oxyanion	Freundlich					
	GAC-CTAC			Virgin GAC		
	$k_F$	$1/n$	$R^2$	$k_F$	$1/n$	$R^2$
Perchlorate	17.35	0.73	0.66	1.69	0.67	0.88
Bromate	21.23	0.71	0.73	2.05	0.63	0.72
Arsenate	11.30	0.56	0.80	1.82	0.42	0.42
Nitrate	16.52	0.62	0.66	1.46	0.58	0.89
Sulfate	9.32	0.74	0.83	2.36	0.67	0.92
Phosphate	15.30	0.52	0.91	2.77	0.69	0.80

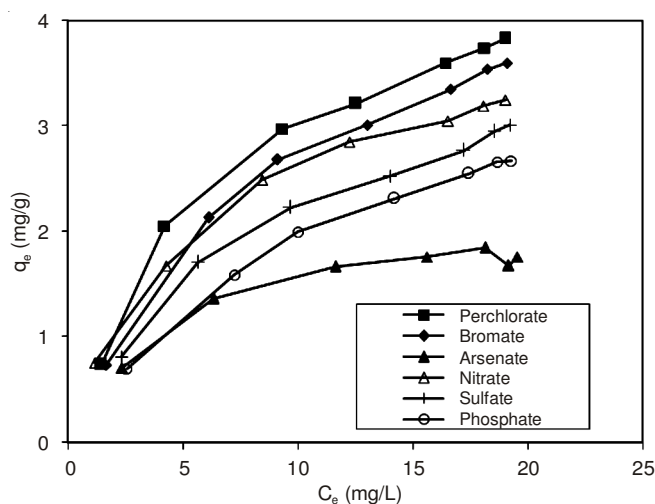


Fig. 2. Adsorption isotherms of oxyanions for virgin GAC

If ion exchange is the main mechanism, the equivalent ratio between chloride released into solution and anion adsorbed on surface should be close to 1:1.

Fig. 3 is the equivalent ratio of chloride released and anion adsorbed. As shown in Fig. 3, for perchlorate, bromate, nitrate or sulfate, at low adsorption the equivalent ratio between chloride released and anion adsorbed was greater than 0.9. As the amount of anion adsorbed increased, the ratio dropped to 0.75-0.80. This indicates that ion exchange did play a significant role in adsorption. Also, ion exchange may be the preferable means of adsorption. At low surface coverage, when many of adsorption sites were available, most of the adsorption was through ion exchange. As surface coverage increased, ion exchange sites became gradually saturated. Adsorption by electrostatic attraction or surface complexation increased. Compared to perchlorate, bromate, nitrate and sulfate, ion exchange played a smaller role in the removal of arsenate and phosphate. The ratio between chloride released and anion

adsorbed was 0.82-0.85 at low surface coverage and 0.60 at high surface coverage. Zeng *et al.*<sup>21</sup> reported that phosphate and arsenate formed inner-sphere complexes with the surface functional groups by an iron oxide-based sorbent. Tang *et al.*<sup>22</sup> argued that the methyl group attached to the quaternary ammonium functional groups of a hydrogel led to the hydrophobicity of the structure, arsenate was adsorbed through electrostatic interaction. Ion exchange accounted for about 60 % of arsenate and phosphate adsorption by GAC-CTAC at high surface coverage. A greater portion of arsenate and phosphate was adsorbed through surface complexation or electrostatic attraction than perchlorate and bromate.

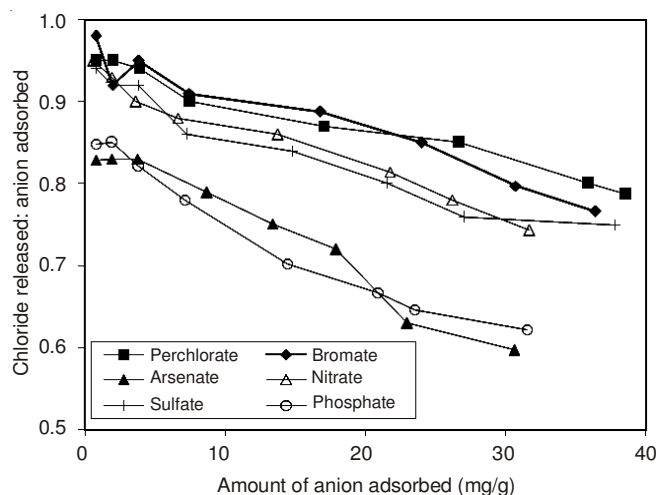


Fig. 3. Equivalent ratio of anion adsorbed vs. chloride released at different surface coverage

**Free energies of adsorption:** The free energy of adsorption was calculated from Langmuir adsorption constant  $b$  by eqn. (4)<sup>23</sup>.

$$\Delta G_{\text{ads}}^0 = -2.303 RT \log b \quad (4)$$

TABLE-3  
FREE ENERGIES OF OXYANION ADSORPTION FOR GAC-CTAC AND VIRGIN GAC

Oxyanion	GAC-CTAC		Virgin GAC	
	b (L/mmol)	$\Delta G_{\text{ads}}^0$ (kJ/mol)	b (L/mmol)	$\Delta G_{\text{ads}}^0$ (kJ/mol)
Perchlorate	30.85	-19.23	11.94	-13.91
Bromate	35.81	-20.07	14.07	-14.83
Arsenate	18.33	-16.31	12.69	-14.25
Nitrate	21.08	-17.10	8.68	-12.12
Sulfate	52.98	-22.29	8.82	-12.21
Phosphate	20.37	-16.90	8.73	-12.16

b in eqn. (4) is adsorption constant from Langmuir equation though in unit of L/mmol. Table-3 lists the free energy of adsorption. According to the free energies, interaction between virgin GAC and various oxyanions were quite similar, with free energy ranging from -14.83 to -12.16 kJ/mol. Mahmudov and Huang<sup>24</sup> proposed that hydrogen bonding between oxyanions and surface function groups may be responsible for anion adsorption by granular activated carbon. The free energies of adsorption by virgin GAC were well within the energy of hydrogen bonding. The free energy of adsorption was much higher with GAC-CTAC. This could be attributed to the fact that with GAC-CTAC, ion exchange played a significant role in adsorption. In general, ionic bonding is stronger than hydrogen bonding. In addition, sulfate exhibited the highest affinity for GAC-CTAC with the largest free energy of adsorption. This may be due to the fact that sulfate exists as divalent ion at the pH studied, thus a higher charge density while others are all monovalents. Among monovalent ions, perchlorate and bromate showed the highest affinity while arsenate and phosphate were the weakest adsorbed ions. The negative values of adsorption free energy meant that adsorption was thermodynamically favorable.

**Adsorption selectivity:** Distribution coefficient on GAC-CTAC reflects the distribution of oxyanions between the surface of activated carbon and solution. The higher the distribution coefficient, the higher the oxyanion's tendency to surface. Table-4 shows distribution coefficients at three different initial concentrations.

TABLE-4  
DISTRIBUTION COEFFICIENTS OF  
OXYANIONS ON GAC-CTAC

Oxyanion	$K_d$ (L/g)		
	Initial concentration (mmol/L)		
	0.01	0.1	1
Perchlorate	70.57 ± 0.60	1.74 ± 0.03	0.046 ± 0.001
Bromate	70.55 ± 0.85	1.75 ± 0.04	0.044 ± 0.001
Arsenate	26.61 ± 0.98	0.22 ± 0.02	0.005 ± 0.002
Nitrate	56.00 ± 1.20	1.53 ± 0.03	0.031 ± 0.001
Sulfate	48.50 ± 1.03	0.86 ± 0.01	0.022 ± 0.003
Phosphate	39.91 ± 1.26	0.69 ± 0.03	0.011 ± 0.001

At all experimental conditions, the distribution coefficients followed the order of perchlorate ≈ bromate > nitrate > sulfate > phosphate > arsenate. GAC-CTAC showed high selectivity for perchlorate and bromate.

Chitrakar *et al.*<sup>18</sup> found that anion selectivity on a cetylpyridinium chloride (CPC)-modified organo-montmorillonite (CPC-mont) followed the order of free energy of hydration of

the anions. The free energies of hydration for nitrate, perchlorate, bromate, sulfate and phosphate are -300, -205, -330, -1080 and -465 kJ/mol respectively<sup>25</sup>. It is believed that the higher the free energy of hydration is, the easier the transport for the anions from aqueous phase to activated carbon surface<sup>26</sup>. Combining free energy of hydration with free energy of adsorption (Table-3), perchlorate and bromate not only are relatively easier to transport from solution to surface but also are high in affinity with surface. In contrast, even though sulfate has the highest surface affinity, its low hydration energy makes its diffusion to surface difficult. Therefore, sulfate is not as competitive as perchlorate and bromate. Arsenate and phosphate showed the weakest adsorption with GAC-CTAC and weakest selectivity.

## Conclusion

Cetyltrimethylammonium chloride modification was effective in enhancing virgin GAC's adsorption of oxyanions. GAC-CTAC showed adsorption capacities 4-7 times those of virgin GAC. Ion exchange was proven to be the main mechanism of adsorption with GAC-CTAC while virgin GAC may adsorb through hydrogen bonding between surface functional groups and oxyanions. The difference in mechanism of adsorption with or without CTAC modification was reflected in the difference in free energies of adsorption. Moreover, studies of distribution coefficients revealed that GAC-CTAC's adsorption of oxyanions were selective. GAC-CTAC showed stronger selectivity towards perchlorate, bromate and nitrate than arsenate, sulfate and phosphate. The difference in selectivity was related to oxyanion's free energies of hydration and adsorption. In general, GAC-CTAC was more selective towards oxyanion with low hydration energy and high adsorption energy. Overall, GAC-CTAC appeared to be a promising candidate in the removal of anions such as perchlorate, bromate and nitrate.

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