Selective Removal of Cr (VI) and Cr (III) in Aqueous Solution by Surface Modified Activated Carbon

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Abstract

The adsorption and reduction of Cr (VI) to Cr (III) by surface modified activated carbon (AC) in an aqueous solution was studied. The effects of surface modifications on the properties of the carbons were investigated by the analysis of specific surface area, carbon surface pH, acid/base surface values and functional groups. In order to understand the Cr(VI) adsorption and reduction ratio from Cr(VI) to Cr(III), the Cr adsorption capacity of AC was also measured and discussed by using inductively coupled plasma and UV spectrophotometer. The modifications bring about substantial variation in the chemical properties whereas the physical properties such as specific surface area, pore volume and pore size distribution nearly were not changed. Total Cr adsorption efficiency of as-received activated carbon (R-AC) and nitric acid treated activated carbon (N1-AC and N2-AC) were recorded on 98.2, 99.7 and 100%. Cr(III) reduction efficiency of R-AC increased largely from 0.4% to 28.3% compared to N1-AC and N2-AC.

Keywords : Chromium, Adsorption, Surface modification, Functional group, Desorption, Activated carbon

1. Introduction

Chromium is introduced into natural waters by a variety of industrial wastewaters including those from leather tanning, textile, electroplating, metal finishing, and chemical industries. Chromium, which is on the top priority list of toxic pollutants as defined by the EPA(Environmental Protection Agency), present as Cr(VI) in the form of oxidized species, such as chromates (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$) and bichromate ($HCrO_4^{-}$), depending on the pH and Cr(VI) concentration [1]. Due to its high solubility, Cr(VI) is most hazardous, since it can accumulate in the food chain and cause several ailments. Once accumulated in high levels, chromium can generate serious problems and, when concentration reaches 0.1 mg/g body weight, it can ultimately become lethal [2]. The strict environmental regulation related to the discharge of heavy metals makes it necessary to develop efficient processes for Cr(VI) removal from wastewater. Currently, the most common methods of chromium removal are adsorption, membrane filtration, ion exchange, liquid-liquid extraction, electrodialysis, reverse osmosis and chemical reactions that involve reduction and precipitation [3].

Among these methods adsorption has been shown as a feasible alternative method for removing traces of chromium from aqueous solution. A review on activated carbons and low cost adsorbents for the adsorption of chromium has been reported recently [4]. Many commercial activated carbons have been used as received and also after chemical modifications for Cr(VI) and Cr(III) adsorption. Important contributions were made by Huang and coworkers [5-7] and also by other groups [8-12]. The dominating mechanism for Cr(VI) removal in most of the studies is surface reduction of Cr(VI) to Cr(III) followed by adsorption of Cr(III). Rivera-Utrilla and Sanchez-Polo [11] analysed the effect of oxygenated surface groups on Cr(III) sorption using a series of ozonised activated carbons. They found that adsorption capacity of the oxidized carbon was greater than that of the original carbon. This effect is due to the formation of surface oxygen groups that, through their ionization, increases their attractive electrostatic interactions between the surface of the activated carbon and the metallic cation present.

Surface modifications of coconut shell AC and coconut shell charcoal with chitosan and oxidizing agents (such as sulphuric acid and nitric acid) were carried out in many studies. The oxidized adsorbents perform better. Nitric acid oxidized AC had higher adsorption capacity than sulphuric acid oxidized AC [13].

This present paper aims the effect of functional groups on the surface reduction of Cr(VI) to Cr(III) during the adsorption process in an surface modified AC. Also, attempts were made to desorb the chromium from adsorbent and the changes of surface characteristics were investigated.

2. Experimental

2.1. Sample Preparation

Coconut based granular AC (30×80 mesh size, Eurim carbon co.) was used for the study. The AC was washed with distilled water and dried in an oven at 110°C for overnight. The washed AC was treated with 1.0 M and 2.0 M nitric acid separately for one hour at 100°C. Nitric acid treated AC was washed with the distilled water until there is no change of pH and then dried in an oven at 110°C for 24 h. The composites were denoted as R-AC, N1-AC and N2-AC to the nitric acid mole concentration.

2.2. Surface area and pore structure

Specific surface area, pore size distribution and pore structure were analyzed by using N_2 adsorption (ASAP 2020, micromeritics, USA) at 77 K [14] and were obtained by BET equation and DFT method. The samples were degassed for 6 h at 473 K in less than 10^{-3} torr. The apparent BET specific surface area was extracted from the linear region in the range of relative pressure ($P/P_0 = 0.05 \sim 0.20$). Correlation coefficient value was adjusted to 1 as soon as possible. The amount adsorbed was converted to liquid volume by assuming a molar volume of liquid nitrogen of 35 $cm^3 mol^{-1}$.

2.3. Surface properties

The elemental analysis of adsorbents was carried out with elemental analyzer (EA1110, CE Instrument, Italy). IR spectra were recorded in FT-IR Prestige-21 (Simadzu, Japan). The pH measurement of the prepared samples was done as per ASTM D 3838 method. Sample (0.5 g) was immersed in distilled water (20 ml) at pH 7, mixed for 12h, and filtered with a nylon membrane filter (0.45 μm in diameter). The pH of the filtrate was measured by using a pH meter. The surface functional groups were investigated according to Boehm titration [15, 16]. Carbon sample (1 g) was placed in the following solution (50 ml) : sodium hydroxide (0.1 mol/L), sodium carbonate (0.05 mol/L), and sodium bicarbonate (0.1 mol/L) respectively. The bottles were sealed and shaken for 24 h, the mixture was filtered subsequently. The excess base was titrated with 0.1 mol/L HCl. The value of acidic sites was determined under the assumptions that NaOH neutralizes carboxylic, lactonic and phenolic groups; that Na_2CO_3 neutralizes carboxylic and lactonic groups; and that $NaHCO_3$ neutralizes only carboxylic groups. At the same time, 0.1 mol/L.

NaOH solution was titrated with 0.1 mol/LHCl as the blank experiment. The mass of surface acid functional groups (SAFG) was calculated by following equation:

$$= \frac{0.1 \times f \times (T_b - T) \times 50 / 20}{w} (mmol/g) \qquad (1)$$

where, T_b (ml) is the titration mass of 0.1 mol/L HCl for the blank experiment, T (ml) the mass of 0.1 mol/L HCl consumed in different filtered solution, w (g) the mass of activated carbon that is equal to 1.0 g in this experiment, and f is the constant.

2.4. Chromium adsorption analysis

Cr(VI) stock solution which has known concentration and pH was prepared and used for the study. AC (1 g) was added to Cr(VI) solution (200 ml, 5 ppm concentration). The mixture was agitated at 150 rpm and allowed to settle. The mixture was then filtered. About portion of filtered solution was used to measure Cr(VI) spectrophotometrically by using UV–Vis spectrophotometer (Optizen 2120UV, MECASYS, Korea) [17], total adsorbed chromium was measured by ICP-AES (Atomscan-25, Thermo Jarrell Ash, USA). In order to determine the concentration of dissolved Cr(VI), Method 7196 was used in this study. This method was determined colorimetrically by reaction with phenylcarbazide in acid solution. A red-violet color of unknown composition is produced. The reaction is very sensitive, the absorbancy index per gram atom of chromium being about 40,000 at 540 nm. Excessed addition of diphenylcarbazide yields the red-violet product, and its absorbance were measureed photometrically at 540 nm.

3. Results and discussion

In order to investigate elemental composition of the as received and acid treated ACs, elemental analysis was carried out. The results of elemental analysis were presented in Table 1. As shown in Table 1, when the more nitric acid concentration was used, the content of nitrogen and oxygen were increased from 0.05 to 0.8%, from 2.1 to 10.1%

Table 1. Elemental Analysis of the Activated Carbons

Samples	C	H	O	N
AC-R	93.6	0.5	2.1	0.05
N1-AC	88.2	0.6	8.6	0.4
N2-AC	84.4	0.6	10.1	0.8

Table 2. Pore Structure of the Activated Carbons

Samples	$S_a(m^2/g)$	$V_b(cm^3/g)$	$V_c(cm^3/g)$	$W_d(nm)$
R-AC	1046	0.347	0.344	0.59
N1-AC	1008	0.355	0.346	0.60
N2-AC	1044	0.383	0.352	0.62

a: BET specific surface area, b: Total pore volume by DFT method, c: Micropore volume by DFT method, d: Average pore width= $2V_{total}/S$
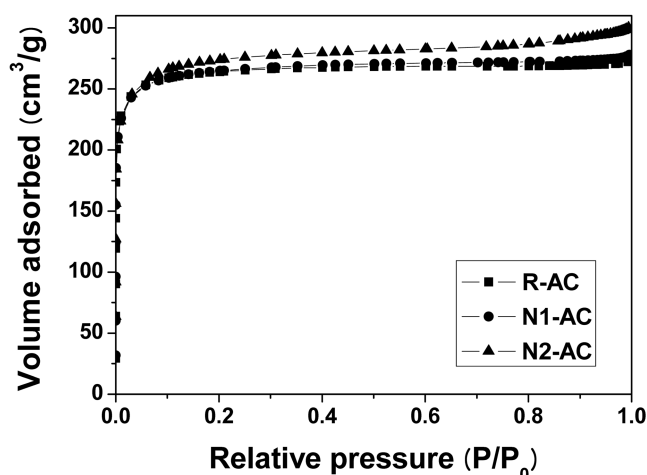
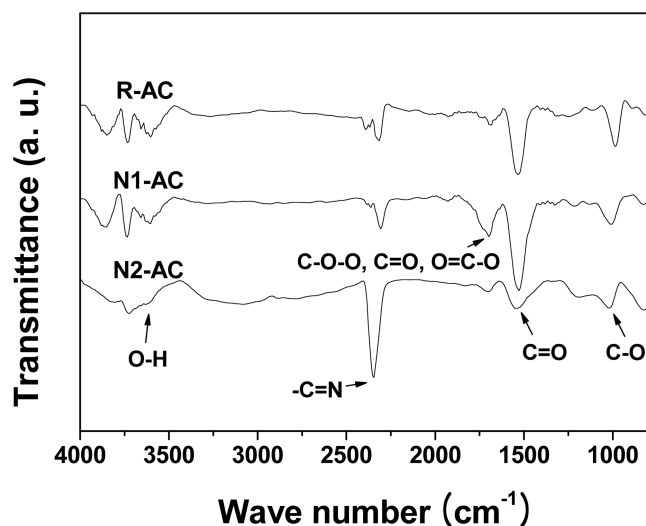**Fig. 1.** Nitrogen adsorption isotherms of non-treated and acid treated activated carbons.

Fig. 2. FT-IR spectrum of non-treated and acid treated activated carbons.

respectively. From these results, it can be known that elemental content is increased with increasing the concentration of nitric acid treatment.

The physical characteristics of the as received and nitric acid oxidized AC are presented in the Table 2, determined by applying BET equation to the N_2 adsorption isotherm at 77 K. The results show that there was a slight increase in the total pore volume, micro pore volume and average pore width after treating with nitric acid. But, there is no

significant change of pore structure. As shown in Fig. 1, all of isotherms divided two regions positively. One is below the relative pressure ($P/P_0 \leq 0.05$). In this region of all of samples, N_2 gas is adsorbed close to total volumes absorbed weight. And very little gas absorbed to residual relative pressure ($0.05 \leq P/P_0 \leq 1$). It means that all samples almost have micropore.

In order to determine the presence of surface functional groups in the activated carbons, FT-IR spectra analysis were carried out. The spectra for non-treated and nitric acid treated AC are shown in the Figure 2. The spectrum results reveal that bands in the region of $1860 - 1650\ cm^{-1}$ are attributed to the $C=O$ stretching vibrations corresponding to the carbonyl and carboxyl groups [18]. The presence of functional group $C - O$, $C = O$ were recorded in all the ACs. In the region $2300\ cm^{-1}$ the N2-AC presents more pronounced bands than the original carbon. These clearly indicate that the oxidation by HNO_3 generates a large number of surface functuinal groups such as carbonyl, carboxyl and nitrate groups.

pH and acid/base value of carbon can be used as a more straight forward approach to compare the chemical properties of carbons. The carbon surface pH can be determined as an approximate measure of the pH at the point of zero charge (pH_{PZC}) [19]. Table 3 presents the pH value of ACs. According to a study by Wang and Lu [20], the difference between the carbon surface pH and pH_{PZC} is less than 2% for most of the carbons that are treated by acids. It is revealed from the Table 3 that the pH values for the carbons are different, ranging from 3.88 (N2-AC) to 7.68 (R-AC). The nitric acid treatment of AC greatly reduces the carbon pH values. It is known that stronger acidic functional groups are deprotonated at a lower pH while weaker acidic functional groups are deprotonated at higher pH [19].

Table 3 also shows the Boehm titration results of the surface properties of the ACs used in this study. It is clearly seen that the nitric acid treatment influence the pH and acid/base surface values of the ACs. Nitric acid treated ACs have more functional groups than them of R-AC. Total acid value and acid functional groups increased with higher nitric acid concentration. The surface pH, acid surface value and base surface value of the nitric acid treated AC samples show large changes compared with them of R-AC. These results represent that nitric acid treatment lead on strong acid reaction. But, by contrast with acid value, base value of nitric acid treated ACs decreased compared that of R-AC.

In order to evaluate the effect of aqueous phase pH, Cr

Table 3. pH, Acid-base Values and Results of Boehm's Titration of ACs Modified by before and after Acid Treatment

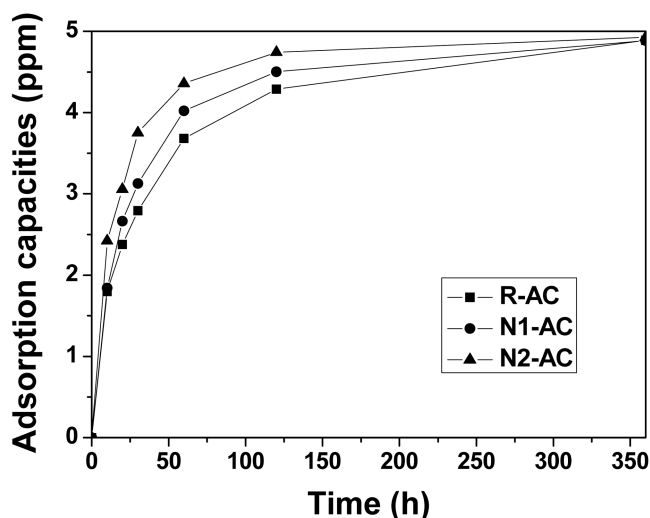|	pH	Carboxyl (meq/g)	Lactonic (meq/g)	Phenolic (meq/g)	acid value (meq/g)	Base value (meq/g)
R-AC	7.68	0.01	0.12	0.73	0.86	0.31
N1-AC	4.33	0.47	0.26	1.56	2.30	0.06
N2-AC	3.88	0.54	0.41	1.51	2.46	0.05

Fig. 3. Cr(VI) adsorption efficiency of non-treated and acid treated activated carbons.
(condition: 5 ppm, 200 ml, 1 g, 150 rpm, pH 3)

Fig. 4. Cr speciation in the adsorbent and the aqueous phase with respect to pH.
Where 1: Cr(VI) adsorption of R-AC, 2: Cr(III) reduction of R-AC, 3: Cr(VI) adsorption of N1-AC, 4: Cr(VI) reduction of N1-AC, 5: Cr(VI) adsorption of N2-AC, 6: Cr(VI) reduction of N2-AC
(condition: 5 ppm, 200 ml, 1 g, 150 rpm, time 12 h)

(VI) adsorption studies were carried out at pH of the range of 3-7. Hence further experiments were carried out at aqueous pH of 3.0, which is similar to reported results [9]. Cr(VI) adsorption efficiency of ACs is shown in the Fig 3. As can be seen in Fig. 3, all of isotherm of samples represent type I (Langmuir type). In case of physical absorption, Langmuir isotherm indicates that the nature of material is consisted of micropore. This type shows rapid adsorption at initial time. It indicates that optimum time for removal of 5 ppm of Cr(VI) is about 2 h at room temperature.

The plot of concentration of Cr(VI), Cr(III) and total chromium concentration in the aqueous phases is depicted in the Fig. 4 and represented in the Table 4. The adsorption of Cr(VI) is maximal at the lowest value of pH (pH 3). Removed total chromium of chemical treated ACs is no significantly change by pH of chromium solution. But, total chromium removal of R-AC was decreased from 98.2 to
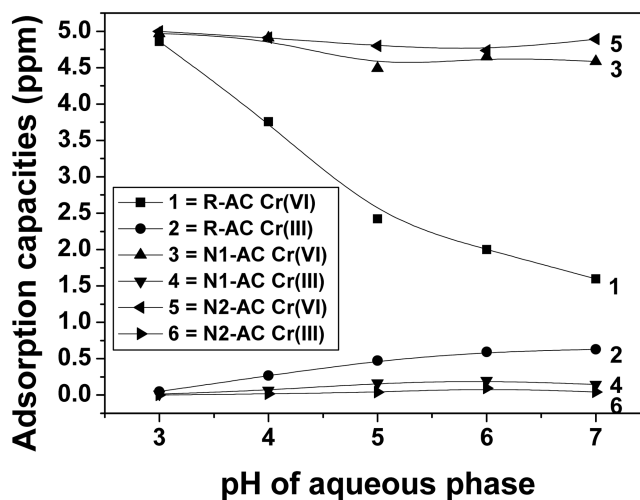
44.56% with increasing pH of chromium solution. According to the change of chromium solution pH from 3 to 7, Cr(VI) concentration and Cr concentration removed by R-AC, N1-AC and N2-AC have maximum in the pH 3. When the pH is 3, Cr(VI) removal efficiency of all samples also is best(99.6, 99.7 and 100% respectively). Reduction from Cr(VI) to Cr(III) was decreased with increasing concentration of nitric acid treatment, whereas reduction from Cr(VI) to Cr(III) was increased with increasing pH. Reduction efficiency from Cr(VI) to Cr(III) of N1-AC and N2-AC changed slightly with increasing pH. But that of R-AC increased largely compared to N1-AC and N2-AC. The result reveals that Cr(VI) content of only R-AC is dependent by Cr solution pH. Also, removal efficiency of Cr(III) was

Table 4. Cr Speciation Removed by using Prepared ACs in Various pH

pH		R-AC			N1-AC			N2-AC		
		Cr(VI)	Cr(III)	Cr_{total}	Cr(VI)	Cr(III)	Cr_{total}	Cr(VI)	Cr(III)	Cr_{total}
pH 3	R	4.860	0.050	4.910	4.971	0.014	4.985	5.000	0	5.000
	(E)	(99.6%)	(0.4%)	(100%)	(99.7%)	(0.3%)	(100%)	(100%)	(0%)	(100%)
pH 4	R	3.757	0.270	4.027	4.912	0.065	4.977	4.911	0.017	4.928
	(E)	(93.3%)	(6.7%)	(100%)	(98.7%)	(1.3%)	(100%)	(99.7%)	(0.3%)	(100%)
pH 5	R	2.424	0.474	2.898	4.492	0.166	4.658	4.800	0.040	4.840
	(E)	(83.6%)	(16.4%)	(100%)	(96.4%)	(3.6%)	(100%)	(99.2%)	(0.8%)	(100%)
pH 6	R	2.000	0.594	2.594	4.650	0.202	4.852	4.737	0.096	4.833
	(E)	(77.1%)	(22.9%)	(100%)	(95.8%)	(4.2%)	(100%)	(98.0%)	(2.0%)	(100%)
pH 7	R	1.598	0.630	2.228	4.585	0.145	4.730	4.893	0.045	4.938
	(E)	(71.7%)	(28.3%)	(100%)	(96.9%)	(3.1%)	(100%)	(99.0%)	(1.0%)	(100%)

R: Removed Cr concentration by absorbent (ppm), E: Efficiency = Removed Cr/Removed Cr_{total} 100%.
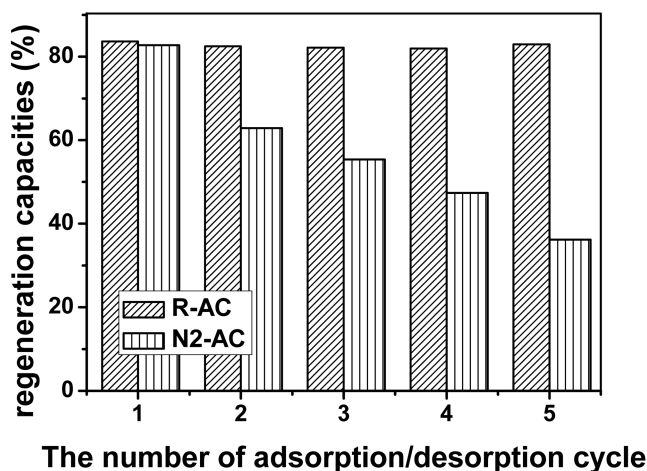(Experimental condition: 5 ppm, 200 ml, 1 g, 150 rpm, time 2 h)

Fig. 5. Regeneration capacities of R-AC and N2-AC. (condition: 0.1 g, 50 ppm, 50 ml, pH 3, adsorption time 6 h, desorbed reagent KOH 0.1 M, desorption time 3 h)

increased with lower pH and higher concentration of nitric acid treatment. Cr(III) removal efficiency of R-AC and N2-AC were recorded 0.4% and 0% at pH 3 respectively, and Cr(III) removal efficiency of R-AC and N2-AC was recorded 28.3% and 1.0% at pH 7 respectively. It shows that selective removal of Cr(VI) and Cr(III) was approximately influenced by pH and concentration of nitric acid treatment. The reduction of Cr(VI) oxyanions is accomplished by a large amount of proton consumption in the acidic solution. This confirms the decisive role played by H^+ in Cr(VI) removal. The Cr(VI) removal from aqueous phase in the ACs occurred through reduction of Cr(VI) to Cr(III) and Cr(VI) adsorption, resulting in predominant attachment of Cr(VI) species with less Cr(III) species.

Desorption studies help to elucidate the mechanism of adsorption for providing the recycling possibility of the carbons. R-AC and N2-AC were desorbed with 0.1 N KOH solution. Regeneration of used carbons is helpful for the recovery of metal ions and reuse of the carbons. As shown Fig. 5, in the first cycle adsorption capacities of Cr(VI) was 80.6%, 81.5% by R-AC and N2-AC, respectively. During the recycling experiment of R-AC and N2-AC adsorbed 92.9% and 36.11% of Cr(VI). It expected KOH act both to remove already adsorbed chromium ions and to add functional group as −OH. So regeneration of R-AC represented higher capacity than initial adsorption. But, although N2-AC indicated more adsorption capacity than R-AC, regeneration capacity of N2-AC show lower than that of R-AC. Because, when desorption was carried out using 0.1 N NaOH, NaOH functional group of N2-AC makes impurity which is toxic to adsorption Cr(VI).

4. Conclusions

The treatment of AC with nitric acid significantly changes the chemical properties of the carbon, such as surface pH and acid-base value, while the specific surface areas are not changed so much. The FT-IR studies indicate that the HNO_3 modifications generate a significantly large number of surface functional groups such as carbonyl, carboxyl and nitrate groups. Cr(VI) removal from aqueous phase occurred through reduction from Cr(VI) to Cr(III) and Cr(VI) adsorption, resulting in predominant attachment of Cr(VI) species. It is evident from analyzing the total chromium and Cr (VI) concentration in the aqueous solution. The reduction takes place without the addition of any external reducing agents. The adsorbed metal can be desorbed by using KOH. Regeneration capacity of R-AC is better than that of N2-AC.

5. References

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