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Remediation of Cr(VI) via combined self-reduction and adsorption by chemically modified carbon sorbents

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Abstract: Hexavalent chromium, Cr(VI), is a highly toxic species, while trivalent chromium, Cr(III), is an essential trace element for humans and other organisms. In the present work, a simple, rapid, and efficient procedure for water treatment of Cr(VI) is described. Active carbon (AC) was chemically treated with HCl and NaOH for the formation of surface modified Acidic-AC and Basic-AC sorbents, respectively. In addition, AC sorbent was treated with HNO_3 as an oxidizing agent and sodium sulfite as a reducing agent for the formation of Ox-AC and Rd-AC sorbents, respectively. The modified AC sorbents were tested to identify their potential applications in removal of Cr(VI) under various controlling factors using the batch technique. The results indicated that these sorbents can be used in water treatment due to their excellent and efficient reduction of Cr(VI) into Cr(III) with percentage transformation values in the range of 90%–100%. Acidic-AC was found to be the superior sorbent in the reduction process of Cr(VI). The produced Cr(III) was removed from aqueous solutions via adsorption on the surface of these sorbents. The reduction and adsorption processes of Cr(VI)-Cr(III) were evaluated and optimized under different experimental parameters. The potential applications of these sorbents in real water treatment were also explored.

Key words: Cr(VI), active carbon, reduction, adsorption, water treatment

1. Introduction

Chromium environmentally exists in several oxidation states, the most common ones being trivalent, Cr(III), and hexavalent, Cr(VI). Trivalent chromium is an essential element for humans and some other organisms and is characterized by its lower toxicity than that of the hexavalent species, which is recognized as a carcinogenic and mutagenic agent.[1] In addition, hexavalent chromium is categorized as one of the most dangerous heavy metal species and inorganic water pollutants and is commonly documented as one of the priority pollutants by the US Environmental Protection Agency. The maximum level of total allowed chromium species concentration was set as 0.1 mg L^{-1} in drinking water.[2] Moreover, the maximum level of hexavalent chromium in drinking water is 0.05 mg/L as set by the World Health Organization standards.[3] The most commonly existing Cr(VI) species are in the forms of dichromate ($Cr_2O_7^{2-}$), hydrochromate ($HCrO_4^-$), or chromate (CrO_4^{2-}) depending on the solution pH values.[4] These hexavalent chromium species are highly soluble and mobile in water and possess a great threat to the quality of surface and ground waters.

The rapid industrialization and development in industrial processes have led to major concern about

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treatment of wastewater in industrial areas. The generated wastewaters from the pigments, leather, metal cleaning, dyes, plating, and mining industries are generally characterized by undesirable amounts of Cr(VI). Therefore, high priority must be given to treating and regulating Cr(VI) disposal at the discharge points. Several methodologies and technologies are usually adopted to remove Cr(VI) from industrial wastewaters. These include precipitation, membrane filtration, solvent extraction, ion exchange, and various biological processes as well as adsorption and biosorption on various adsorbents and biosorbents.[5–11] The choice of treatment methods of hexavalent Cr(VI) from various water matrices is mainly dependent on several important factors. A common chemical treatment method for remediation of Cr(VI) concentrations is generally based on reduction of Cr(VI) to Cr(III) by using various selected reducing agents such as hydrogen sulfide (H_2S),[12] sodium dithionite ($Na_2S_2O_4$),[13] sulfur dioxide (SO_2) or sodium metabisulfite ($NaHSO_3$), calcium metabisulfite ($CaHSO_3$), calcium polysulfide (CaS_5),[14] ferrous sulfate ($FeSO_4$) or Fe(II) ion,[15] or Fe(0) or tin(II) chloride ($SnCl_2$).[16] The reduction process is commonly followed by Cr(III) precipitation under the action of an alkaline medium or by using some adsorbents to bind with the produced Cr(III). However, these treatment methods are now considered undesirable due to the application of multistep reactions, high use of toxic and expensive chemicals, and the production of large amounts of chemical sludge.[17] An alternative methodology for treatment of Cr(VI) in various water and wastewater matrices was accomplished by sorption-based processes, wherein sorption of chromium species on various native and chemically modified active carbon (AC) adsorbents has been the subject of several recently published papers.[18–22] Such frequent applications of AC sorbents are mainly due to the high surface area, high adsorption capacity, high adsorption rate, and high specific surface reactivity. The identified maximum adsorption capacity of AC is commonly dependent on several important factors, such as type of raw materials, loaded surface functional groups, and nature of the pore structure. In addition, the activation process is well known as one of the important factors in determining the reactivity of produced AC sorbents because different activation methods of the same raw materials may produce different physical and chemical characteristics of AC adsorbents.[23–25] Sorbents based on active carbons are commonly prepared from various raw materials such as wood, charcoal, petroleum coke, sawdust, and coconut shell and all of these materials are characterized by high carbonaceous contents. Active carbon sorbents are generally activated by thermal decomposition in a high-temperature oxidation condition for the production of some active surface oxygen functional groups. The physical and chemical properties of AC adsorbents are mainly determined on the basis of activation process as well as the oxygen treatment for adjusting the quality of surface functional groups such as hydroxyl, carboxyl, and phenolic groups. Thus, the reactivity of AC sorbents is mainly based on the possible alteration in the final carbon surfaces.[26,27]

In this work, four different AC sorbents were synthesized based on chemical treatment and surface modification by using HCl, NaOH, HNO_3, and Na_2SO_3 to obtain four modified AC sorbents with various acidic, basic, oxidizing, and reducing surface properties. The efficiency of these four AC sorbents for possible self-reduction-adsorption process of Cr(VI) from various water samples was studied, explored, and compared with untreated AC sorbent. Optimization of all experimental controlling factors and implementation in real water treatment were also explored and evaluated.

2. Results and discussion

2.1. Surface characterization

Surface functionality of carbon sorbent is characterized by its responsibility for all activity and reactivity as well as capability for adsorption properties and processes. In this work, infrared spectroscopy was used to obtain information about the chemical structure and functional groups of the raw material and the chemically modified AC sorbents. The FT-IR of AC sorbent is represented in Figure 1, which shows a few characteristic peaks that are mainly related to the organic nature of AC.[28,29] However, upon redox treatments of AC, these peaks were

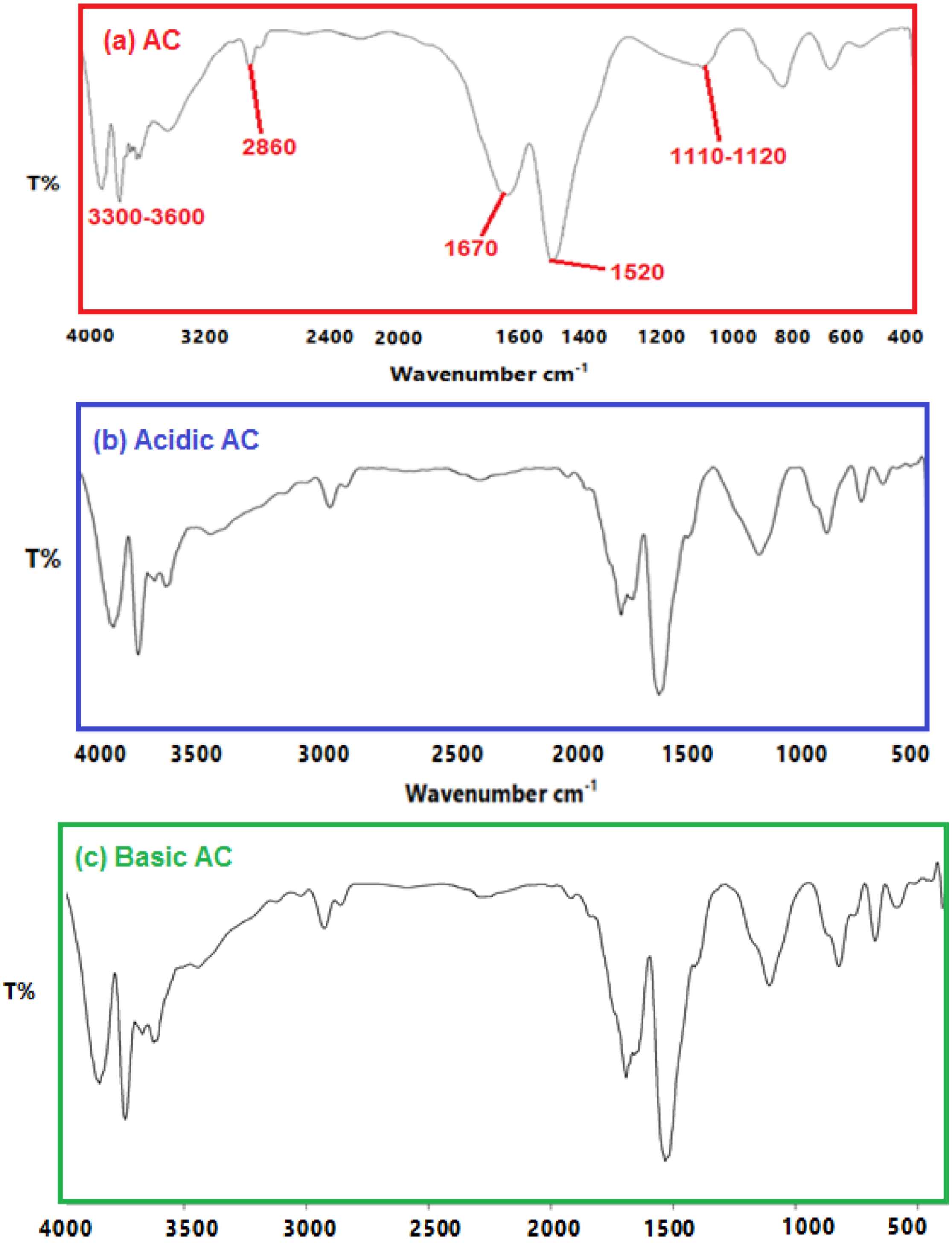

Figure 1. FT-IR spectra of different AC adsorbents: a) AC, b) Acidic-AC, and c) Basic-AC.

intensified and other new IR peaks were produced. A peak centered at 1110–1120 cm^{-1} is mainly due to $\nu_{(C-O)}$ of the methoxy group. The strong bands appearing at 1520 and 1670 cm^{-1} are ascribed to the formation of oxygen functional groups based on highly conjugated C=O stretching in the carboxylic or carboxylate group as well as the carbonyl group. A peak was observed at 2860 cm^{-1} and ascribed to the presence of aliphatic compounds. A broad band in the region of 3300–3600 cm^{-1} is typically attributed to $\nu_{(O-H)}$ stretching or an adsorbed water molecule.[28] Thus, the redox treatment process of the AC surface is important in improving and intensifying the various functional groups of the AC sorbent. The FT-IR spectra of surface-modified AC sorbents, Acidic-AC, Basic-AC, Ox-AC, and Rd-AC, were also found to exhibit similar FT-IR peaks.[29]

Scanning electron microscopy (SEM) is also a useful and efficient technique in evaluation of the surface morphology. Figure 2 represents the SEM image of blank AC sorbent; upon chemical treatment of AC, the surfaces of all sorbents were slightly changed by various chemical reagents. However, the particles retained their original shapes and distribution.

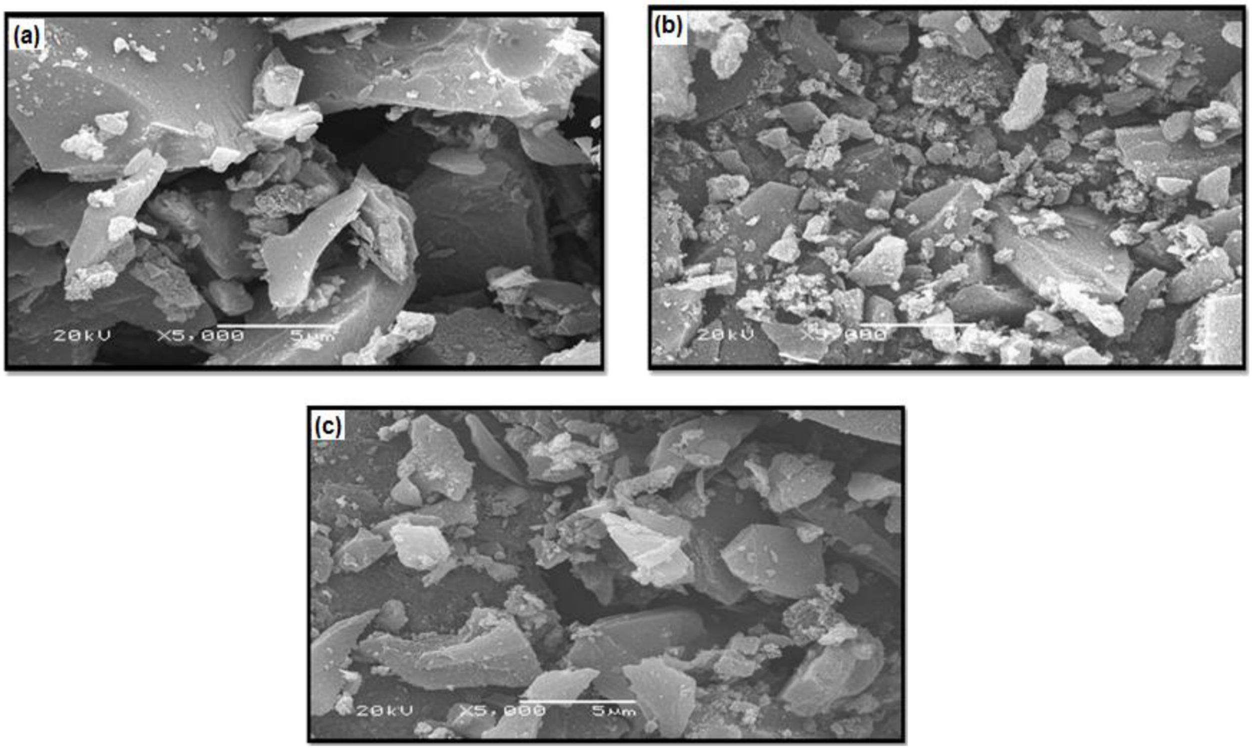

Figure 2. SEM images of a) AC, b) Acidic-AC, and c) Basic-AC.

2.2. Remediation of Cr(VI) via reduction by various modified active carbon sorbents

2.2.1. Effect of pH

The reduction process and reaction of Cr(VI) by the action of native and modified AC sorbents may be accomplished via the strong oxidizing power of Cr(VI) as well as the presence of some functional groups on the surface of carbon materials such as an olefinic double bond (C=C), carbonyl (C=O), and hydroxyl (OH) as well as other oxidizable functional groups. In addition, carboxylic, phenolic, and lactonic groups also persist along with the previous oxidizable groups and the existence of these functional groups is heavily dependent on the processes of carbon activation.[30] Therefore, the tendency of AC or chemically modified AC sorbents to be involved in redox reaction with Cr(VI) is mainly related to the presence of some of these oxidizable functional groups.

Table 1 compiles the percentage values of Cr(VI) reduction into Cr(III) by modified AC sorbents, Acidic-AC, Basic-AC, Ox-AC, and Rd-AC, in the presence of various buffering conditions. The results of the reduction process are also compared with those determined by AC sorbent. It is evident from the listed data that AC sorbent produced excellent percentages of Cr(VI) reduction, 96%, 95%, and 93%, in acidic pH values of 1.0, 2.0, and 3.0, respectively. This behavior is mainly due to the ability of Cr(VI) to convert into Cr(III) in low pH values ($\text{pH} \leq 3.0$).[31–33] On the other hand, Acidic-AC sorbent was found to maintain excellent percentage values of Cr(VI) reduction, as listed in Table 1. These values are characterized in the range of 92%–97% in the pH range of 1.0–10.0. This trend indicates that the treatment of AC with an acid such as HCl will be in favor of the reduction reaction of Cr(VI). In other words, AC-treated acid was characterized by a high retention of its reduction efficiency for Cr(VI) even with the pH change of the reaction from 1.0 to 10.0. The only observed change in the percentage of Cr(VI) reduction was identified in highly basic solutions with pH 11.0 and 12.0 as found at 65% and 8%, respectively.

Table 1. Effect of pH on the percent reduction values of Cr(VI) into Cr(III).

pH	Percent reduction of Cr(VI) into Cr(III) by different AC sorbents*				
	AC	Acidic-AC	Basic-AC	Ox-AC	Rd-AC
1	96	97	94	82	94
2	95	95	94	78	92
3	93	94	94	70	85
4	54	94	78	69	77
5	52	94	33	69	60
6	40	94	20	58	55
7	28	94	17	49	53
8	20	94	6.0	81	25
9	16	93	3.0	80	19
10	16	92	3.0	79	15
11	16	65	3.0	52	6.0
12	3.0	8.0	3.0	47	6.0

*Percentage extraction values are based on triplicate analysis with $\pm(\leq 1.0\%)$.

Basic-AC sorbent was also found to behave similarly to the AC sorbent in the reduction process of Cr(VI) into Cr(III). The highest percentage reduction value was obtained as 94% in strongly acidic solutions (pH 1.0–3.0). However, starting from pH 5.0 to pH 12, the percentage values of Cr(VI) reduction were found to decrease more than those of the AC sorbent. In this case, two factors are working and controlling the reduction reaction of Cr(VI) by this sorbent. The first is based on the AC matrix, which is working as a good reducing agent for Cr(VI) in lower pH values without any contribution of the surface-loaded base on Basic-AC. The second is the strong contribution of the loaded base due to the strong inhibition of the reduction of Cr(VI) to the minimum value in higher pH values of contact solutions.

The effect of surface loading with oxidizing and reducing agents such as HNO_3 and Na_2SO_3 for the formation of Ox-AC and Rd-AC, respectively, was also studied and the results are compiled in Table 1. The role of HNO_3 as an oxidizing agent in the reduction process of Cr(VI) by Ox-AC sorbent was detected in low pH values (≤ 3.0) in which the percentage of the reduction process was lowered to 70%–82%. The presence of nitric acid on the surface was found to inhibit the efficiency of activated carbon sorbent to act as a good reducing agent. The opposite behavior was observed in the case of Rd-AC in which Na_2SO_3 was loaded on the AC adsorbent. The contribution of reducing agent was identified in the pH range of 4–7 as the values of the percentage of reduction were increased compared to those of AC sorbent.

The conclusion that can be drawn from the effect of pH value as well as the effect of surface modification on the reduction of Cr(VI) by AC sorbents can be summarized in the following points. AC sorbent is a good reducing agent for reduction of Cr(VI) in pH $\leq$ 3.0. Acidic-AC is the most efficient sorbent for reduction of Cr(VI) in acidic, neutral, and basic solutions (pH 1.0–10.0). Basic-AC and Ox-AC are less efficient as a sorbent for Cr(VI) reduction.

2.2.2. Effect of contact time

The effects of contact time on the percentage of Cr(VI) reduction by all AC sorbents were also studied in three different representative buffer solutions (pH 1.0, 5.0, and 11.0) and the results of this study are compiled in Table 2. The selected time interval values were 1.0, 5.0, 10.0, 15.0, 20.0, 25.0, and 30.0 min. The effect of reaction time on the reduction process of Cr(VI) was found to exhibit an insignificant contribution in the solution with pH 1.0 for all AC sorbents except Ox-AC. The percentage reduction values of Cr(VI) were identified as 94% after 1 min of reaction time and 96% after 30 min of reaction time for the untreated AC sorbent. This trend indicates that the reduction process of Cr(VI) is independent of the contact time value. The same behavior was also characterized in the case of Acidic-AC, Basic-AC, and Rd-AC sorbents. However, the effect of reaction time on the reduction process of Cr(VI) by Ox-AC sorbent was found to enhance the percentage values of reduction from 70% to 82% upon increasing the time from 1.0 to 30.0 min, respectively. This indicates that the AC sorbent loaded with oxidizing agent requires more time to act as an efficient reducing adsorbent for Cr(VI). In acidic solutions with pH 5.0, the reaction time showed no contribution to the reduction process of Cr(VI) in the case of Acidic-AC and Basic-AC sorbents due to maintaining the percentage reduction values at 92%–94% and 26%–33%, respectively. The other three adsorbents were affected by changing the time of reaction from 1.0 to 30.0 min as they produced gradual increases in the percentage of reduction from 30% to 52%, 46% to 69%, and 20% to 60% for AC, Ox-AC, and Rd-AC sorbent, respectively. However, in basic solution with pH 11.0, all activated carbon sorbents were found to exhibit almost no change in the percentage values of Cr(VI) reduction upon changing the reaction time from 1.0 min to 30.0 min, as listed in Table 2.

2.2.3. Effect of sorbent dosage

The effect of sorbent dosage on the percentage of Cr(VI) reduction by AC, Acidic-AC, Basic-AC, Ox-AC, and Rd-AC was also studied as an important contributing factor in this process.[34] The selected sorbent dosages were used in the range of 0.025–0.250 g. Three different Cr(VI) solutions were adjusted to pH 1.0, 5.0, and 11.0 and the results of this study are shown in Table 3. It was found that, in solutions with pH 1.0, the increase in sorbent dosages of AC, Acidic-AC, Basic-AC, and Rd-AC AC from 0.025 to 0.250 g exhibited no contribution to the percentage of Cr(VI) reduction. This behavior may be attributed to the strong reducing power of the AC matrix, while the only sorbent that exhibited slight dependence on the adsorbent dosage was Ox-AC. This behavior also confirms the role of HNO_3 as an oxidizing agent in the inhibition of the reduction process of Cr(VI). It is evident that the percentage values of Cr(VI) reduction increase as the sorbent dosage increases in the case of AC, Basic-AC, Ox-AC, and Rd-AC sorbents in solution with pH 5.0. On the other hand, the

Table 2. Effect of time on the percent reduction values of Cr(VI) into Cr(III).

pH	Time (min)	Percent reduction of Cr(VI) into Cr(III) by different AC sorbents*				
		AC	Acidic-AC	Basic-AC	Ox-AC	Rd-AC
1	1	94	97	94	70	93
	5	94	97	94	75	94
	10	94	97	94	78	94
	15	94	97	94	79	94
	20	96	97	94	82	94
	25	96	97	94	82	94
	30	96	97	94	82	94
5	1	30	92	26	46	20
	5	31	92	33	48	25
	10	44	92	33	49	60
	15	45	94	33	51	60
	20	52	94	33	69	60
	25	52	94	33	69	60
	30	52	94	33	69	60
11	1	14	61	3.0	52	5.0
	5	15	65	3.0	52	6.0
	10	15	65	3.0	52	6.0
	15	15	65	3.0	52	6.0
	20	16	65	3.0	52	6.0
	25	16	65	3.0	52	6.0
	30	16	65	3.0	52	6.0

*Percentage extraction values are based on triplicate analysis with ±(≤1.0%).

Acidic-AC sorbent was found to be less affected by the change in the adsorbent dosage as the percentages of Cr(VI) reduction values were maintained in the range of 90%–98%. In the case of solutions with pH 11.0, the change in sorbent dosage was characterized by a good contribution to the reduction process of Cr(VI) by AC, Acidic-AC, Ox-AC, and Rd-AC sorbents. This may be attributed to the resistance of these sorbents to the basic solutions when 0.025 g of sorbent was used, leading to inhibition of the reduction process of Cr(VI) to percentage values of 3%, 61%, 52%, and 4% for the examined four sorbents, respectively. Upon increasing the sorbent dosage to 0.025 g of AC, Acidic-AC, Ox-AC, and Rd-AC sorbents, the percentage reduction values were found to reach the maximum percentages of 30%, 98%, 90%, and 51%, respectively. This conclusion can be also confirmed by the obtained reduction results of Cr(VI) by Basic-AC sorbent. This sorbent was found to be strongly unaffected by the change of dosage due to the presence of basic solution (pH 11.0) and a surface loaded with a basic compound (NaOH). The identified percentage values of Cr(VI) reduction by Basic-AC sorbent were 2.0% and 8.0% in the presence of 0.025 and 0.250 g of sorbent dosage, respectively.

2.2.4. Effect of initial Cr(VI) concentration

The effect of initial concentration of Cr(VI) on the reduction process by various examined sorbents was also explored and evaluated[35] in this section by using six different concentrations, 20.0, 40.0, 50.0, 60.0, 80.0, and 100.0 mg L^{-1}. The results of this study are compiled in Table 4 in the form of mg L^{-1} values of reduced Cr(VI) into Cr(III) in the presence of three different buffering conditions, pH 1.0, 5.0, and 11.0. It is clear from the identified results of Cr(VI) reduction at pH 1.0 for all five examined sorbents that a gradual increase in

Table 3. Effect of sorbent dosage on the percent reduction values of Cr(VI) into Cr(III).

pH	Mass (g)	Percent reduction of Cr(VI) into Cr(III) by different AC sorbents*				
		AC	Acidic-AC	Basic-AC	Ox-AC	Rd-AC
1	0.025	95	95	94	70	93
	0.05	95	97	94	80	94
	0.075	96	97	94	82	94
	0.1	96	97	94	82	94
	0.15	96	97	94	82	94
	0.2	96	97	94	82	94
	0.25	96	97	94	82	94
5	0.025	41	90	16	49	33
	0.05	45	90	19	58	44
	0.075	48	90	25	64	49
	0.1	52	94	33	69	60
	0.15	60	95	37	78	64
	0.2	79	97	45	83	64
	0.25	82	98	51	88	75
11	0.025	3.0	61	2.0	52	4.0
	0.05	6.0	65	3.0	52	7.0
	0.075	15	65	3.0	52	6.0
	0.1	16	65	3.0	52	6.0
	0.15	20	71	5.0	86	6.0
	0.2	23	93	7.0	89	21
	0.25	30	98	8.0	90	51

*Percentage extraction values are based on triplicate analysis with ±(≤1.0%).

the mg L^{-1} of reduced Cr(VI) was detected as the concentration of Cr(VI) increased. This behavior is mainly due to the presence of a great number of metal ions in solution compared to the accessible mass of sorbent. In addition, the maximum reduced amounts of Cr(VI) into Cr(III) were obtained in the case of AC, Acidic-AC, Basic-AC, and Rd-AC sorbents by producing 98.0, 97.0, 97.0, and 97.0 mg L^{-1}, respectively, out of the 100.0 mg L^{-1} initial concentration of Cr(VI). The lowest values of Cr(VI) reduction were obtained in the case of Ox-AC sorbent due to the opposed retardation of loaded oxidizing agent to the reduction process. The same trends and behaviors were also observed for Acidic-AC, Basic-AC, and Rd-AC in pH reduction of Cr(VI) in this buffering condition.

2.2.5. Effect of coexisting ions on Cr(VI) reduction by various sorbents

The effect of interfering cations such as Na$^+$, K$^+$, Ca^{2+}, and Mg^{2+} as well as anions such as Cl , Br$^-$, and SO$_4^{2-}$ in the form of NaCl, KBr, MgSO$_4$, and CaCl$_2$ (0.025 g of each salt) were also studied to evaluate the reduction process of hexavalent chromium in aqueous solutions by all AC sorbents.[36] This study is important in examining the effectiveness of various AC sorbents to exhibit possible reduction reactions in aqueous solutions that contain some metal salts, as in the case of real water samples. In this study, 0.025 g of sample of the interfering salt was added to Cr(VI) and the experiment was completed under the optimum conditions. The collected results of this study in three different buffering solutions with pH values of 1.0, 5.0, and 11.0 are listed in Table 5. At pH 1.0, an identical or slight increase in the results of Cr(VI) reduction was obtained. This indicates no direct interaction or contribution of the interfering ions in the reduction process. In pH 5.0

Table 4. Effect of initial Cr(VI) concentration on the reduction process by various sorbents.

pH	mg L^{-1} Cr(VI)	Cr(VI) reduced into Cr(III) (mg L^{-1}) by different AC sorbents*				
		AC	Acidic-AC	Basic-AC	Ox-AC	Rd-AC
1	20	18	18	18	18	18
	40	38	38	37	34	37
	50	48	49	47	41	47
	60	58	58	58	45	57
	80	78	78	78	59	78
	100	98	97	97	68	97
5	20	16	19	9.0	15	6.6
	40	34	38	16	28	20
	50	26	47	17	35	30
	60	27	52	17	29	44
	80	28	68	19	34	64
	100	27	81	22	37	89
11	20	4.4	14	2.0	16	2.8
	40	8.0	26	3.2	32	4.8
	50	8.0	33	1.5	40	7.5
	60	6.0	27	1.8	46	3.6
	80	4.8	12	1.6	58	2.4
	100	2.0	5.0	1.0	61	1.0

*Percentage extraction values are based on triplicate analysis with ±($\leq$1.0%).

solution, the interfering ions or salts were found to affect and decrease the percent of reduction in the case of AC, Acidic-AC, Ox-AC, and Rd-AC. This behavior may be due to the possible blocking of the active sites on the surface of AC sorbent via direct reaction between the interfering cation and the surface functional groups. Finally, in solution with pH 11.0, one can conclude that no general trend was observed, whereas some salts exhibited higher Cr(VI) reduction or lower Cr(VI) reduction than other salts as listed.

Table 5. Effect of coexisting species on the percent reduction values of Cr(VI) into Cr(III).

pH	0.025 g of interfering salt	Percent reduction of Cr(VI) into Cr(III) by different AC sorbents*				
		AC	Acidic-AC	Basic-AC	Ox-AC	Rd-AC
1	NaCl	98	97	98	90	99
	KBr	99	97	99	98	98
	$CaCl_2$	98	97	100	92	99
	$MgSO_4$	99	97	99	90	97
	Cr(VI)	96	97	94	82	94
5	NaCl	14	74	62	44	18
	KBr	36	72	60	45	23
	$CaCl_2$	47	75	58	49	26
	$MgSO_4$	35	73	59	46	25
	Cr(VI)	52	94	33	69	60
11	NaCl	10	45	11	76	14
	KBr	8.0	52	12	78	11
	$CaCl_2$	12	78	26	82	17
	$MgSO_4$	14	52	20	79	15
	Cr(VI)	16	65	98	52	6.0

*Percentage extraction values are based on triplicate analysis with ±($\leq$1.0%).

2.2.6. Removal of Cr(III) as the reduction product of Cr(VI) by AC sorbents

The ability of various chemically modified AC sorbents to extract and remove Cr(III), as the reduction product of Cr(VI), was also studied in an attempt to accomplish a full water treatment and removal of all chromium species. The identified metal uptake capacity values of Cr(III) by all sorbents were determined in this study. AC, Acidic-AC, and Rd-AC sorbents were found to produce metal sorption capacity values of Cr(III) of 900, 900, and 880 μmol g^{-1}, respectively. The highest metal capacity value was found as 990 μmol g^{-1} in the presence of Basic-AC, which demonstrates the contribution of the loaded base in the extraction process of Cr(III). On the other hand, the lowest metal capacity value was detected as 630 μmol g^{-1} in the case of Ox-AC. This result supports our finding about the less contribution of this sorbent in the reduction process of Cr(VI) into Cr(III).

2.2.7. Applications of modified AC sorbents for reduction and remediation of Cr(VI) from real water samples

The ability of chemically modified AC sorbents to remediate and extract Cr(VI) from real samples such as sea water and industrial wastewater was further studied as the final step to explore the potential applications of these sorbents in water treatment. This study was accomplished by adjusting the real water samples to pH 1.0 via addition of HCl solution and allowing this solution to run over the selected AC sorbent loaded in the initial step of microcolumn technique in which Cr(VI) was reduced to Cr(III). The collected effluent was then adjusted to pH 7.0 by using NaOH solution and allowed to run over a second stage of microcolumn in which Cr(III) was adsorbed on the surface of packing activated carbon sorbents. The net results of this remediation process of Cr(VI) and Cr(III) are compiled in Table 6 for the five examined AC sorbents. It is evident from this study that the combined percentage values of reduction and extraction of Cr(VI) were in the ranges of 91%–96% and 92%–96% for the two tested sea water and wastewater samples, respectively, by the five AC adsorbents. These values signify the validity and generality of the proposed method as an efficient water treatment procedure via combined reduction and extraction of Cr(VI) from various water samples and matrices.

Table 6. Application of AC adsorbents in real water treatment.

Sample	Cr(VI) (mg L^{-1})	Sorbent mass	% Cr(VI)*
			reduction removal
Sea water	2.27	100 mg AC	91
		100 mg Acidic-AC	90
		100 mg Basic-AC	93
		100 mg Ox-AC	92
		100 mg Rd-AC	96
Wastewater	3.21	100 mg AC	94
		100 mg Acidic-AC	94
		100 mg Basic-AC	95
		100 mg Ox-AC	92
		100 mg Rd-AC	96

*Percentage extraction values are based on triplicate analysis with ±(≤1.0%).

3. Experimental

3.1. Chemicals and solutions

Active carbon, potassium chromate, sodium acetate, sodium hydroxide, sodium sulfite, and other metal salts were purchased from Aldrich Chemical Company (St. Louis, MO, USA) and Adwic Chemicals (Alexandria, Egypt) and used as received. Nitric acid and hydrochloric acid were all of analytical grade and purchased from Aldrich Chemical Company and BDH Limited (Poole, UK). Doubly distilled water (DDW) was used in all preparations and in washing of the apparatus.

3.2. Synthesis of modified active carbon sorbents

A sample of 7.5 g of AC was weighed and transferred to a beaker, and then 0.1 L of HCl solution (2:1 v/v ratio) was added and the reaction mixture was stirred for 4 h. The produced acid-treated AC was filtrated, washed with distilled water, and dried at 60 °C to produce Acidic-AC sorbent. The acid-treated AC sorbent was left to dry in an oven at 60 °C for 24 h. A sample of 7.5 g of AC was weighed and transferred to a beaker, and then 0.1 L of NaOH (1.0 M) was used and added as the basic solution and the reaction mixture was stirred for 4 h. Basic-AC sorbent was filtrated, washed with distilled water, and dried at 60 °C for 24 h.[28,29] Another 7.5 g of AC sample was weighed and transferred to a beaker, and 0.1 L of HNO_3 solution (2:1 v/v ratio) was used as an oxidizing agent, added to the reaction mixture, and stirred for 4 h. The oxidized AC was filtrated, washed with distilled water, and dried at 60 °C for 24 h to produce Ox-AC sorbent.[30] The reduced AC sorbent, Rd-AC, was also prepared in a similar way by using Na_2SO_3 solution (1.0 mol) as the reducing agent.

3.3. Characterization of the adsorbents

A Shimadzu Fourier transform infrared spectrophotometer (FT-IR System-BX 0.8009) was used in the range of 200–4000 cm^{-1} to acquire the FT-IR spectra of activated carbon, modified Acidic-AC, Basic-AC, OX-AC, and Rd-AC sorbents. These sorbents were also imaged by SEM (JSM-5300, JEOL Ltd.). An ion sputtering coating device (JEOL-JFC-1100E) was used to coat the SEM specimens with gold to increase the conductivity.

3.4. Effect of various controlling factors on reduction of Cr(VI) by modified activated carbon sorbents

3.4.1. Effect of pH

A solution of 50.0 mg L^{-1} Cr(VI) was prepared and adjusted to the required pH value in the range of 1.0–12.0 using either HCl or NaOH solutions. Next, 100 ± 1 mg of the dry modified AC sorbent was weighed and added to 25.0 mL of this solution and the mixture was shaken at room temperature for 30.0 min by an automatic shaker. Finally, the mixture was filtrated and unreduced Cr(VI) ion was detected by using UV-Vis spectrophotometric determination at $\lambda_{max} = 420$ nm and the percentage values of Cr(VI) reduction by modified activated carbon sorbents were then identified.

3.4.2. Effect of contact time

A sample of 100 ± 1 mg of dry modified AC sorbent was weighed and added to 25.0 mL of 50.0 mg L^{-1} Cr(VI) solution previously adjusted to pH 1.0, 5.0, and 11.0. This mixture was shaken at room temperature under various shaking time values of 1.0, 5.0, 10.0, 15.0, 20.0, 25.0, and 30.0 min using an automatic shaker. After equilibration, the mixture was filtered and unreduced Cr(VI) ion was detected by using UV-Vis spectrophotometric determination at $\lambda_{\mathrm{max}} = 420$ nm and the percentage values of Cr(VI) reduction by modified activated carbon sorbents were then identified.

3.4.3. Effect of sorbent dose

The effect of sorbent dose was studied by using various amounts of modified AC sorbents in each experiment (0.025, 0.05, 0.075, 0.100, 0.150, 0.200, 0.250 g). The selected sorbent dosage was mixed with 25.0 mL of 50 mg L^{-1} Cr(VI) solution previously adjusted to pH 1.0, 5.0, and 11.0. The above mixture was then shaken at room temperature for 30.0 min by an automatic shaker to examine the effect of mass dosage. The reaction mixture was filtered after equilibration and the reduction process of Cr(VI) into Cr(III) was monitored by determination of unreduced Cr(VI) ion using UV-Vis spectrophotometric analysis at λ_{max} = 420 nm to identify the percentage values.

3.4.4. Effect of initial chromium concentration

Different concentrations of Cr(VI) were prepared (20.0, 40.0, 60.0, 80.0, and 100.0 mg L^{-1}) in the presence of various pH values (1.0, 5.0, and 11.0). Next, 25 mL of these solutions was added to 100 ± 1 mg of the dry modified AC sorbent. The mixture was shaken at room temperature for 30.0 min by an automatic shaker to examine the effect of concentration. Finally, the mixture was filtered and unreduced Cr(VI) ion was detected by using UV-Vis spectrophotometric analysis at λ_{max} = 420 nm as described above.

3.4.5. Effect of interfering ion

Several selected metal salts such as NaCl, KBr, $CaCl_2$, and $MgSO_4$ were used to study the effect of coexisting ions on the reduction process of Cr(VI) by using various modified AC sorbents. A sample of the selected salt (0.025 g) was added and mixed with 25.0 mL of 50.0 mg L^{-1} Cr(VI) at pH values of 1.0, 5.0, and 11.0. The mixture was shaken at room temperature for 30.0 min by an automatic shaker to examine the effect of interfering ion. Finally, the unreduced Cr(VI) was filtered and detected using UV-Vis spectrophotometric analysis at λ_{max} = 420 nm as described above.

3.4.6. Adsorptive removal of the Cr(VI) reduction product, Cr(III), by modified activated carbon sorbents

The following procedure was performed in order to examine and identify the possible adsorption of Cr(III), as the reduction product of Cr(VI), by various modified AC sorbents. A sample of 100 ± 1 mg of dry modified AC sorbent was mixed with 1.0 mL of 1.0 M Cr(VI) and 9.0 mL of buffer (pH 1.0). The mixture was shaken at room temperature for 30 min by an automatic shaker and after complete equilibration the mixture was filtered. Another sample of 100 ± 1 mg of dry modified activated carbon sorbent was added to the filtrate and the whole mixture was adjusted to pH 7.0 and shaken at room temperature for 30 min by an automatic shaker. Finally, the mixture was filtered and washed three times by using DDW. The unretained Cr(III) was then determined by complexometric titration to identify the adsorbed amount of Cr(III) by the various modified AC sorbents. The metal sorption capacity value was calculated from metal mass balance as given in Eq. (1).

$$q = \frac{(C_o - C)\,V}{m} \times 10^3 \tag{1}$$

Here, C_o and C are the initial and residual metal ion concentrations in mol L^{-1}, respectively; V is the aqueous volume of the sorption reaction (L); m is the mass of AC sorbent (g); and q (μmol g^{-1}) is the sorption metal capacity, which represents the amount of metal ion (μmol) adsorbed per gram of dry sorbent.

3.4.7. Applications of modified AC sorbents for reduction and sorptive removal of Cr(VI) from real water samples

Two water samples, sea water and industrial wastewater, were used in this study. A multistage microcolumn technique was used and the mass of packing AC sorbent in each stage was 100 ± 1 mg. One liter of the tested water sample was spiked with $\sim$2.0–3.0 mg L^{-1} of Cr(VI) and adjusted to pH 1.0 by the addition of HCl solution. This solution was passed over a microcolumn in which Cr(VI) was reduced to Cr(III). The collected effluent was then adjusted to pH 7.0 by using NaOH solution and allowed to run over the second stage microcolumn in which Cr(III) was removed from solution via adsorption on the surface of AC packing materials. The collected solution after the second passage was subjected to atomic absorption analysis to identify the percentage values of reduction and removal of Cr(VI) and Cr(III), respectively.

4. Conclusion

The collected results of this study confirm the superiority of modified AC adsorbents compared to the previously reported Cr(VI) remediation studies as listed in Table 7. The simplicity and validity are evident in this study upon using modified AC adsorbents for remediation of toxic Cr(VI) ion into nontoxic Cr(III) species, which was then adsorbed on the surface of these adsorbents. The treated AC adsorbent in the form of Acidic-AC

Table 7. Comparison to other previously reported Cr(VI) remediation studies.

Adsorbent	Remediation process	Studies	Applications	Reference
Zero-valent iron nanoparticles	Adsorption and reduction	Time, pH, and initial concentration	Removal from aqueous solutions	37
$CoFe_2O_4$/activated carbon composite	Adsorption	Time, pH, initial concentration, and temperature	Removal from aqueous solutions	38
Magnetic Fe_3O_4–FeB nanocomposites	Adsorption	Time, pH, and initial concentration	Removal from aqueous solutions	39
NZVI/graphene nanosheets	Adsorption	Time, pH, and initial concentration	Removal from aqueous solutions	40
Gelatin-impregnated yeast	Biosorption	Time, pH initial concentration, dosage, and interfering ions	Adsorptive removal of Cr(VI) from sea water and industrial wastewater	41
Gelatin	Biosorption	Time, pH initial concentration, dosage, and interfering ions	Adsorptive removal of Cr(VI)–Cr(III) species from sea water and tanning industrial wastewater	42
Alumina-functionalized isatin-thiosemicarbazone	Adsorption	Time, pH, distribution coefficient, and separation factor	Adsorptive removal of Cr(VI)–Cr(III) species from sea water and industrial wastewater	43
Chemically treated active carbon sorbents	Adsorption and reduction	Time, pH initial concentration, dosage, and interfering ions	Reduction and adsorption removal of Cr(VI) from sea water and industrial wastewater	This work

was characterized by high superiority as the most effective adsorbent in the remediation process of Cr(VI) with percentage removal values in the range of 92%–97% using pH 1.0–10.0. The second most effective adsorbent was Basic-AC, which gave 78%–94% in the pH range of 1.0–4.0. The potential applications of these sorbents in real water treatment were also explored and the collected results show that the percentage removal values of Cr(VI) from sea water and wastewater samples were in the ranges of 91%–96% and 92%–96%, respectively, using the examined activated carbon adsorbents.

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