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Regeneration of acid-modified activated carbon used for removal of toxic metal hexavalent chromium from aqueous solution by electro kinetic process

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ABSTRACT

Hexavalent chromium Cr(VI) is toxic and readily adsorbed by some adsorbents; therefore, its removal from wastewater is extremely important. Granular activated carbon (GAC) is a well-known adsorbent for the removal of heavy metals from water and wastewater. It has been found that removal rates of Cr(VI) by acid-modified-activated carbon decreases over time and the permeable reactive barriers become almost inefficient. This study aims to investigate the regeneration performance of activated carbon by electrokinetic (EK) process under potential gradient of 5 V cm^{-1}, electrical current of 30–50 mA, and elapsed time of 8 and 24 h. About 95% regeneration efficiency of activated carbon was achieved by an EK system with electrical current of 30–50 mA operated for 24 h, so GAC was successfully regenerated. Also it was shown that only about 80% of regeneration efficiency was achieved by applying EK for 8 h.

Keywords: Permeable reactive barriers; Polluted groundwater; Hexavalent chromium; Granular activated carbon; Electrokinetic process; Regeneration

1. Introduction

The production of heavy metals increased rapidly since the industrial revolution. As a result, pollution of water bodies with heavy metals became a major environmental problem of the modern world. Therefore, in the last decades, the presence of heavy metals in aquatic ecosystems has received widespread attention due to their potential human health risks and harmful effects on other living organisms.

Chromium, which is one of the most toxic and important heavy metals commonly found in wastewater for instance in tanning and electroplating industries. Also it is on the top priority list of toxic pollutants as defined by the US Environmental Protection Agency [1]. Chromium generally exists in water with two stable oxidation states: hexavalent Cr(VI) and trivalent Cr(III) [2]. The most probable Cr(VI) species in aqueous solution are chromates (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), and bichromate ($HCrO_4^-$), depending on pH and Cr(VI) concentration [3].

Cr(VI) is toxic, in contrast, trivalent chromium Cr(III) is much less toxic and immobile and can be readily precipitated out of solution in the form of $Cr(OH)_3$ [4]. Furthermore, Cr(VI) is highly mobile in soil and aquatic systems, and also is a strong oxidant capable of being adsorbed by skin [5]. Human toxicity of Cr(VI) includes lung cancer, as well as kidney,

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liver, and gastric damage [6]. The maximum levels permitted for Cr(III) and Cr(VI) in wastewater are 5 and 0.05 mg L^{-1}, respectively [7].

Permeable reactive barriers (PRBs) are one of the most promising passive treatment technologies, due to its effectiveness regarding various contaminants, and its low cost compared to the other *in situ* technologies [8].

Activated carbon presents a substantial high adsorption capacity for many inorganic contaminants [9] and in the case of Cr(VI), it acts with two mechanisms of adsorption. First Cr(VI) species are adsorbed on the interior surface of the carbon and then reduced to Cr(III), which is adsorbed at the external carbon surface [10]. It was found that granular activated carbon (GAC) in PRB systems is highly suitable for removing Cr(VI) from contaminated groundwater [11–13].

In this work, adsorbents acid-modified GAC were used for the removal of Cr(VI) from wastewater. GAC is a well-known adsorbent for the removal of heavy metals from water and wastewater, but the high cost of it limits its use as an adsorbent in developing countries. Hence, it is not worthwhile to do to replace GAC when it becomes ineffective. Therefore, it is a growing need to find new methods for *in situ* regeneration of acid-modified GAC.

In this study, a novel idea in design of PRB is used to solve the decrease of GAC efficiency which is due to the precipitation of contaminants on carbon surface in PRB, by regenerating and recovering the reactive media.

Electrokinetic (EK) process is one of the innovative technologies for soil remediation. This technology applies a low-level direct current (DC) to the polluted soil by electrodes placed in the ground to remove contaminants from the soil [14], but EK was used in this test to regenerate reactive media in PRB by cleaning up the precipitation contaminants of heavy metals such as Cr(VI).

Recently, EK, operated with low power consumption, was applied to regenerate activated carbon. It was reported that 95% regeneration efficiency of activated carbon saturated with phenol was achieved by an EK system with 0.1 M NaCl as processing fluid under constant current of 100 mA operated for 5 h. Also, it was shown that desorption mechanism occurs in cathode reservoir and, whereas, oxidation degradation was found in anode reservoir. The processing fluid using EK was the dominant factor affecting regeneration performance [15]. It was reported that 99% regeneration efficiency of activated carbon saturated with toluene was achieved with 0.5 M NaOH as processing fluid, which was higher than processing fluid of $NaCO_3$ and Na_2SO_4 [16].

According to previous studies, the present study provides a solution when GAC becomes ineffective using EK method to remove accumulated contaminants such as Cr(VI) anions from the reactive media in PRB, neutralizing negative charges on the surface of the adsorbents by excessive hydrogen ions which produce positive acidic groups. So GAC was regenerated again, and about 95% regeneration efficiency of activated carbon was achieved by application of EK to the PRB layer. EK involves inserting electrodes into the anode and cathode reservoirs that encompass the PRB layer zone, then a DC is applied which was supplied using DC power source with 33 V and 3 A.

2. Materials and methods

2.1. Materials and characterizations

Distilled water was used in all preparations. Potassium dichromate ($K_2Cr_2O_7$) and deionized water were used to prepare synthetic chromium containing wastewater, the solution pH was adjusted to the desired value by adding H_2SO_4 or NaOH.

GAC is widely considered as a suitable adsorbent for onsite or offsite treatment of polluted groundwater. Carbon presents a high adsorption capacity for many organic and inorganic contaminants for its high surface area, due to the microporous structure, and a high degree of surface reactivity caused by surface oxide groups and inorganic impurities [17], used GAC has a grain-size distribution of 0.3–2.36 mm, and it was selected for this study. The properties of it are shown in Table 1, which the density ($r_s = 1.43$ g cm^{-3}), bulk density of active carbon was 0.5 g cm^{-3}.

Uncontaminated silica sand with non-uniform size (mean diameter $d_{50} = 0.65 \pm 0.2$ mm) was used as porous medium, the properties of sand are shown in Tables 1 and 2, which the bulk density is ($r_b =$ 1.703 g cm^{-3}), particle density is ($r_s = 2.62$ g cm^{-3}), average porosity of sand is ($n = 0.35$), and average saturated hydraulic conductivity is ($K = 0.52$ cm s^{-1}). In the control runs with no addition of activated carbons, no removal of Cr(VI) was found over the time period of typical experiments.

2.2. Methods

2.2.1. Preparation of the solution of chromium

A stock solution of 1.0 g L^{-1} was prepared by dissolving 2.8298 g of potassium dichromate ($K_2Cr_2O_7$) in 1.0 L of double-distilled water, which was further

Table 1
The main characteristics of media

Material	Washed sand	Granular activated carbon
Characteristics	$D_{50} = 0.65 \pm 0.2$ mm $\rho = 2.62$ (g cm^{-3}) Porosity ($n = 0.35$)	$D_{50} = 1.85 \pm 0.2$ mm $\rho = 1.43$ (g cm^{-3}) in water Porosity ($n = 0.4$)

Table 2
The characteristics of sand

L.O.I	MgO	CaO	K_2O	Al_2O_3	Fe_2O_3	SiO_2	pH
0.0%	0.24%	0.27%	0.19%	0.95%	0.85%	97.5%	7.5–8

diluted for the preparation of test solutions. Several solutions with different initial concentrations of potassium dichromate were prepared. The required pH was adjusted by addition of 0.4 N H_2SO_4, depending on the acidity of the sample.

2.2.2. Activated carbon preparation

The activated samples were washed with distilled water to remove surface impurities and dried at 100℃, then poured into 0.1 mol L^{-1} HCl (50 g of raw GAC was added into 250 mL of acid solution) and stirred for 1 h to eliminate the residual alkali [18]. Then, the samples were washed with hot distilled water until the pH of the filtrating solution was neutral (pH ~ 6.5) in order to eliminate activating agent residues and other inorganic species formed during the process [19]. The produced GAC was then dried at 105℃ overnight.

2.2.3. Preparation of the uncontaminated sand

Sand was soaked in water for 24 h to dissolve the lumps, then washed on the No 200 sieve until the wash water which was coming through the sieve, became clear, then dried at 105℃. The sand which is used in this study is poorly graded sand. The grain size distribution is shown in Fig. 1.

2.3. Apparatus and instrumentation

The pH values of the solutions were measured by Hanna pH meter using a combined glass electrode, the pH meter was standardized using buffer solutions of pH values: 4, 7, and 10.

The metal ions Cr(VI) were determined by UV–vis spectrophotometer (HACH DR 4000).

The concentration of total Cr in solution was determined by using a flame atomic absorbance spectrometer. Subtracting the Cr(VI) values from the total chromium gave the Cr(III) concentration for each sample.

DC power supply: a DC was used in this tests. DC power supply with 33 V and 3 A was used. The DC power supply can provide variable voltage or variable currents as we needed.

3. Experimental setup

The continuous adsorption studies of Cr(VI) reduction by GAC were conducted in a bench-scaled laboratory setup as shown in Fig. 2, schematically. Uncontaminated sand with non-uniform size (mean diameter $d_{50} = 0.65 \pm 0.2$ mm) was used as a porous medium. The length of the porous medium before and after the PRB position was 10 and 30 cm, respectively. There are several empty compartments separated by movable and perforated walls, one of them before the position of PRB and another one after it for placing electrodes (anode and cathode). The EK method was used to remove accumulated contaminants from the reactive media of PRB and generate H^+ ions.

The laboratory model was made of plexiglass, a main reservoir was provided to supply influent water with certain Cr(VI) concentration into porous medium. A reservoir in up-stream and one in down-stream of porous medium were considered to create a steady-state condition of flow through sand. A certain pore velocity through sand was made with regulation of water level in these reservoirs. Also a DC power supply with 33 V and 3 A as well as two titanium (Ti) electrodes (with a thickness of 1 mm, a width of 2 cm, and a length of 15 cm) were used for applying DC in these tests.

In order to move the precipitated chromate ions away from the PRB layer and towards the contaminated water, a positive electrode was placed before the PRB layer while a negative electrode was placed after it. These positive and negative electrodes filtered

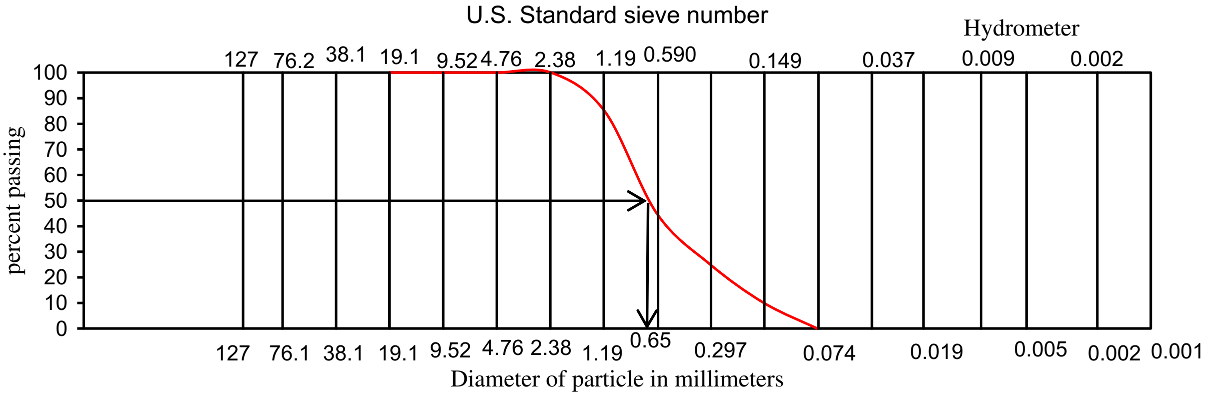

Fig. 1. Grain-size distribution of sand.

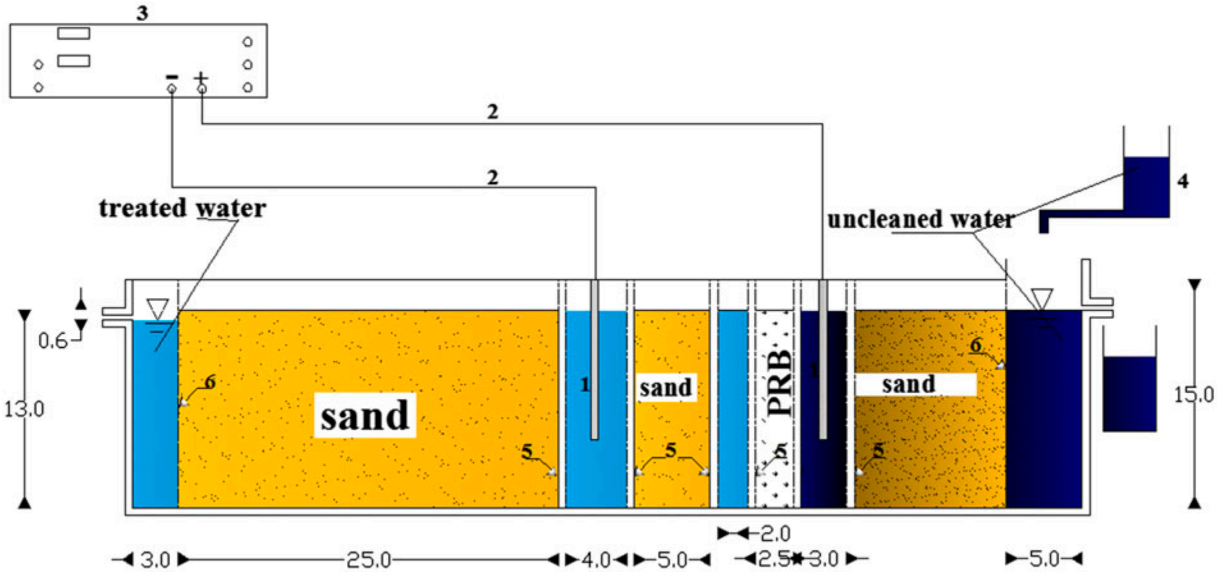

Fig. 2. Schematic laboratory setup: 1-titanium (Ti) electrodes, 2—cable, 3—DC power supply, 4—water tank, 5—perforated walls, and 6—plastic mesh.

out the precipitated chromate ions and drove them away from the filtered water.

4. Experimental procedure

The simulated polluted groundwater with a Cr(VI) was prepared from a stock solution, using deionized water and a solution pH of 4.5, 5.5, 6.5, and 8.0 with the initial Cr(VI) concentration of 12, 19, 26, and 33 mg L^{-1}. Then this is supplied to the entrance compartment, then collected at an exit compartment at the appropriate interval where it is analyzed for Cr(VI) concentration and PH solution. The temperature during the operation was 25 ± 5˚C.

The percentage of Cr(VI) adsorption from aqueous solution was computed by the following equation:

$$\text{Removal efficiency of Cr(VI) (\%)} = [(C_0 - C)/C_0] \times 100 \quad (1)$$

where C_0 and C are the initial and final Cr(VI) concentrations, respectively.

Application of EKs to the PRB layer involves inserting electrodes into the anode and cathode reservoirs that encompass the PRB layer zone, then sending a low DC voltage gradient or current across the electrodes. Electrodes should be located, so they are able to work as cathodes (negatively charged) or anodes

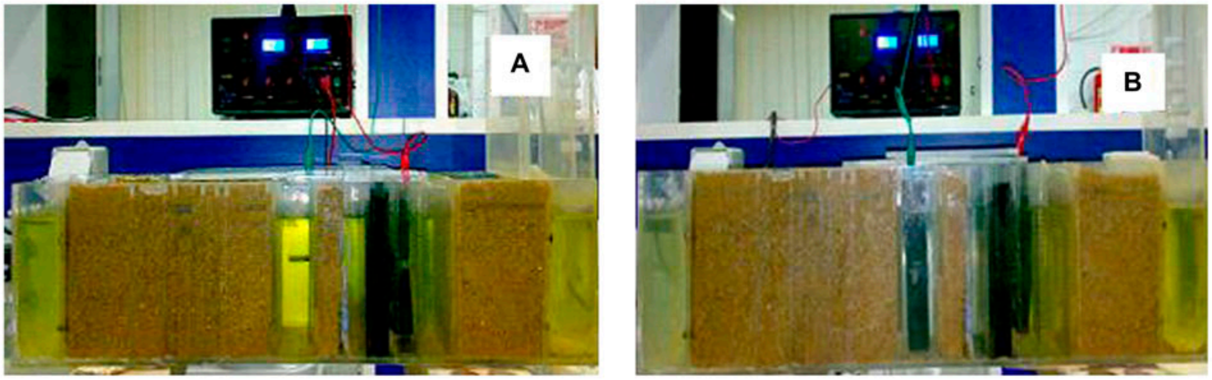

Fig. 3. Laboratory setup with EK system (A: time elapsed of applying EK = 0, B: time elapsed of applying EK = 24 h).

(positively charged), Fig. 3. Under the induced electric potential, electrokinetic ion transport occurs by principal mechanisms, such as electromigration, electroosmosis, and electrophoresis.

The first mechanism electromigration, is the migration of the ions (cations and anions present in the soil and also the H^+ and OH^- produced by the process of electrolysis) toward the electrodes under the influence of an electric potential. The second mechanism which is called electroosmosis consists of the motion of liquid through a porous medium under the influence of an applied electrical field [14].

All experiments were conducted under potential gradient of 5 V cm^{1-} and DC 30–50 mA for 24 or 8 h to study the effect of electrical current on regeneration of the PRB layer.

The current density would be initially increased, owing to electrolysis reaction was occurred, then decreased to a low current density because of clogging of metal precipitates.

Seven experiments were conducted for some states with pH solution ≥4.5 were shown in Table 3.

5. Results and discussion

When GAC was treated with nitric acid, oxygen acidic groups such as –COOH, –OH, –COOR were initially produced and then further reacted with H^+, forming positive hydronium ions such as $–COOH_2^+$, $–OH_2^+$, and $=C=OH^+$ which are schematically shown in Fig. 4. This accounted for the adsorption of Cr(VI) which was more effective in the case of acid treated activated carbons, and resulted with an increase in acidic functional groups [20].

Based on the equilibrium constants for Cr(VI) hydrolysis, $HCrO_4^-$ and CrO_4^{2-} are the two major species in the solution based on the equilibrium constants for Cr(VI) hydrolysis [21]. Adsorption of $HCrO_4^-$and CrO_4^{2-} on GAC may be explained by the following reactions [22,23]:

Table 3
Values of parameters of all experiments

Number test	pH	Initial concentration (mg L^{-1})	Time applying EK (h)	Direct current (mA)
1	4.5	19	24	30–50
1	4.5	19	8	30–50
2	5.5	12	24	30–50
2	5.5	12	8	30–50
3	6.5	12	24	30–50
3	6.5	12	8	30–50
4	6.5	12	24	30–50
4	6.5	12	8	30–50
5	8	19	24	20–30
5	8	19	8	20–30
6	6.5	26	8	30–70
6	6.5	26	24	30–70
7	4.5	33	8	30–50
7	4.5	33	24	30–50

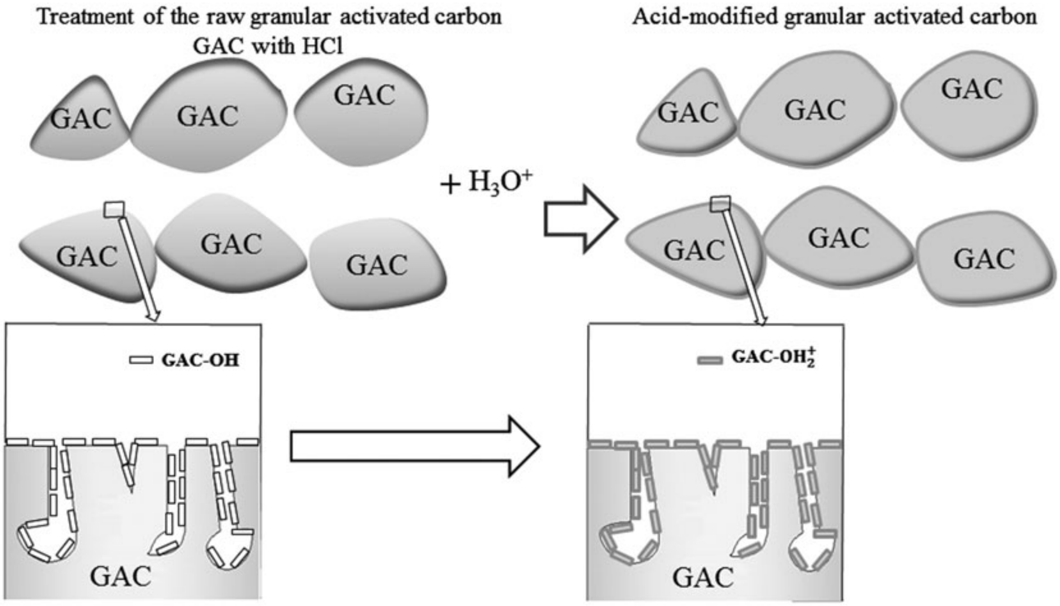

Fig. 4. Schematic diagram illustrating the process of treatment of the raw GAC with HCl.

$$AC–OH_2^+ + HCrO_4^- \leftrightarrow AC–OH_2CrO_4^- + H^+ \qquad (2)$$

$$AC–OH_2^+ + CrO_4^{2-} \leftrightarrow AC–OHCrO_4^{2-} + H^+ \qquad (3)$$

From Fig. 5, it can be seen that the adsorption process proceeds in two stages. High adsorption rates are observed within the first time interval, whereas a decrease in the Cr(VI) adsorption occurs in the second one. The initial rapid removal is due to the availability of the positively charged functional groups of the GAC adsorbent, also initially, the adsorption sites are open and the metal ions interact easily with the sites. Hence, a higher rate of adsorption is observed. The subsequent slower adsorption can be attributed to changes in GAC surface reactivity, due to continuous diminishing of the number of positively charged functional groups throughout the adsorption experiment. Also sufficient active sites occupied by sorbate, so active sorption sites are not sufficiently available for the sorbate to occupy which are schematically shown in Fig. 6, in addition, the electrostatic repulsion between negative charges of adsorbate ions results in decreasing of the adsorption percentage [24]. So we will try to increase the efficiency of reactive media again when the adsorption slows down by using EK which involves applying a low DC to electrodes that are inserted in a compartment anode (positive electrode) before PRB position and in a compartment cathode (negative electrode) after PRB position.

When the PRB (GAC) becomes almost inefficient, DC is applied by inserting electrodes into the anode and cathode reservoirs that encompass the PRB layer zone. When a DC potential is applied to the electrodes, an electrolysis reaction of the water takes place. The hydrogen ions (H^+) generated at the anode compartment due to hydrolysis according to the equation [14]:

$$\text{Anode}: 2H_2O - 4e^- \rightarrow O_2\uparrow + 4H^+ \qquad (4)$$

On the other hand, the production of (OH^-) at the cathode increases the pH value at the cathode, according to the equation:

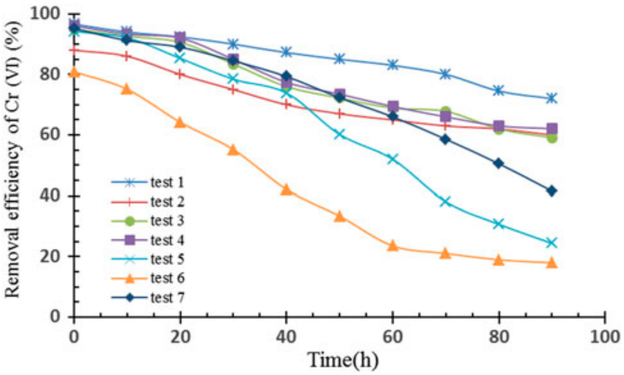

Fig. 5. Variation of the percentage of removal Cr(VI) with time by PRB (GAC).

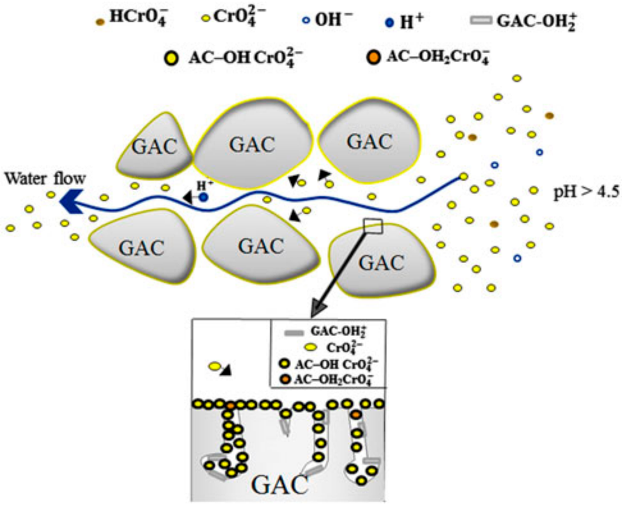

Fig. 6. Schematic representations of the reaction mechanisms for the removal of Cr(VI) by acid modified GAC which is showing the active sites, occupied by sorbate.

$$\text{Cathode}: 4H_2O + 4e^- \rightarrow 2H_2\uparrow + 4OH^- \tag{5}$$

The pH profiles along anode and cathode reservoir for all three states are shown in Fig. 7, the anode pH was acidified due to H^+ produced by electrolysis of the water. Near the cathode end, OH^- was produced by electrolysis of the water resulting in increasing pH.

Acid front produced in the anode compartment advances toward the cathode aided by electroosmosis, and basic front produced at the cathode compartment advances toward the anode by diffusion and ionic migration. The advance of basic front is slower than the advance of the acidic front because of the counteracting electroosmosis flow and also because the ionic mobility of H^+ is about 1.76 times that of OH^- [14]. As a consequence, the acid front dominates the chemistry across the space between the two electrodes except for small sections close to the cathode.

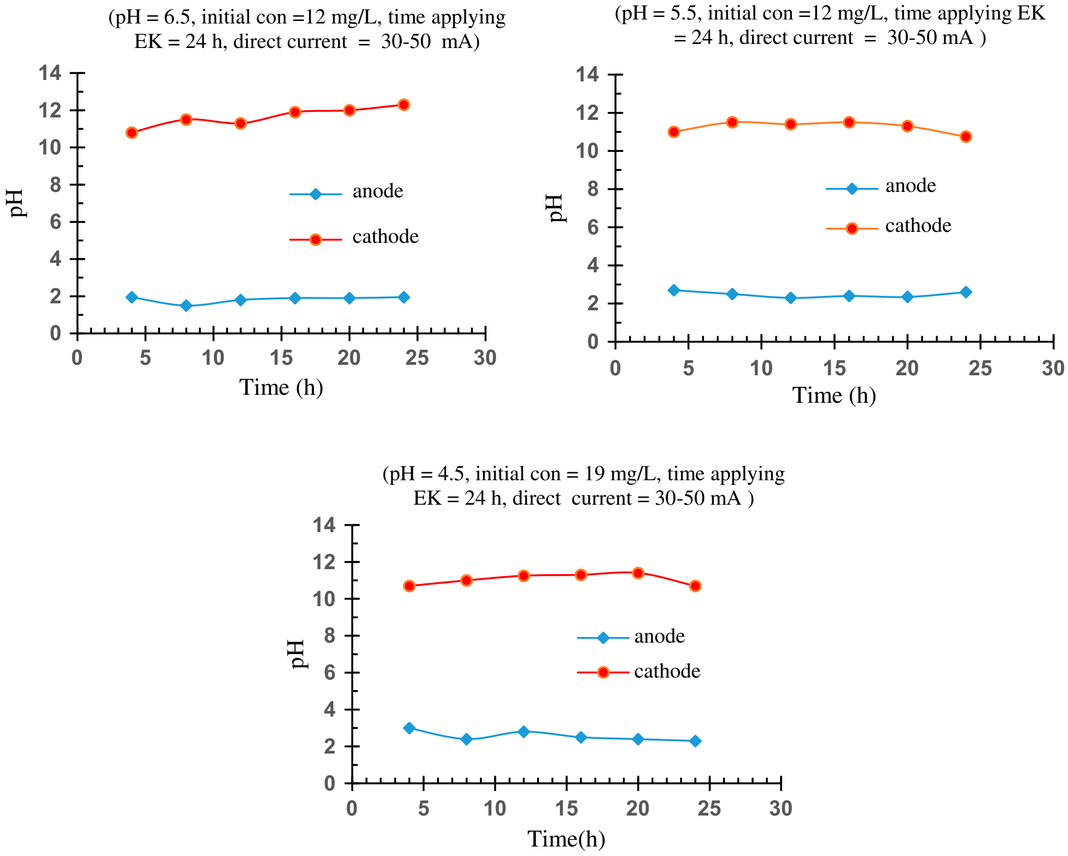

Fig. 7. Variation of the pH values along anode and cathode reservoirs during the test for three states.

When the hydronium ion's concentration increases, the majority of adsorbent surface will be positively charged according to the following equation:

$$\mathrm{GAC-OH}\ +\mathrm{H_3O^+}\rightarrow\mathrm{GAC-OH_2^+}+\mathrm{H_2O}\tag{6}$$

The favorable effect after applying DC potential can be attributed to the neutralization of negative charges on the surface of the adsorbents by increasing hydrogen ions and also production of the amount of acidic functional groups on GAC according to the following equation:

$$\mathrm{AC–OH_2CrO_4^-}+\mathrm{H^+}\rightarrow\mathrm{AC–OH_2^+}+\mathrm{HCrO_4^-}\tag{7}$$

Also when two electrodes are inserted for applying an electrical current, negatively charged ions such as chromate ions travel toward the anode by electromigration flow which are schematically shown in Fig. 8. Then the metal anions are removed, so the adsorption sites become open and the metal ions are able to interact easily with them, hence increasing the adsorption rate of Cr(VI). Also reduction of Cr(VI) to Cr(III) in the anode reservoir under acidic conditions occurs because both the chromate and dichromate anions are strong oxidizing reagents at low pH [25]:

$$\mathrm{Cr_2O_7^{2-}}+14\mathrm{H^+}+6\mathrm{e^-}\rightarrow2\mathrm{Cr^{3+}}+7\mathrm{H_2O}\tag{8}$$

Then Cr(III) cations tried to migrate toward cathode reservoir under DC potential followed by precipitation of $\mathrm{Cr(OH)_3}$ under alkaline conditions. So $\mathrm{Cr^{3+}}$ cations were negligible in the cathode reservoir and also in the sand section after it.

Thus, it was noticed that the concentrations of Cr(III) and Cr(VI) increased in the anode reservoir after applying an electrical current when the initial pH was low. For example at test 1 (pH 4.5) the initial concentrations of Cr(VI) and Cr(III) in the anode reservoir before applying an electrical current were 19 and 3 mg $\mathrm{L^{-1}}$, respectively while after applying electrical current for 24 h, the pre-mentioned initial concentrations were 22.15 and 6.8 mg $\mathrm{L^{-1}}$, respectively. At this test, the concentrations of Cr(VI) and Cr(III) after PRB at time = 90 h (in the cathode reservoir) before applying an electrical current were 4.1 and about 0 mg $\mathrm{L^{-1}}$, respectively whereas after applying an electrical current for 24 h, Cr(VI) and Cr(III) concentrations became 0.66 and about 0 mg $\mathrm{L^{-1}}$, respectively.

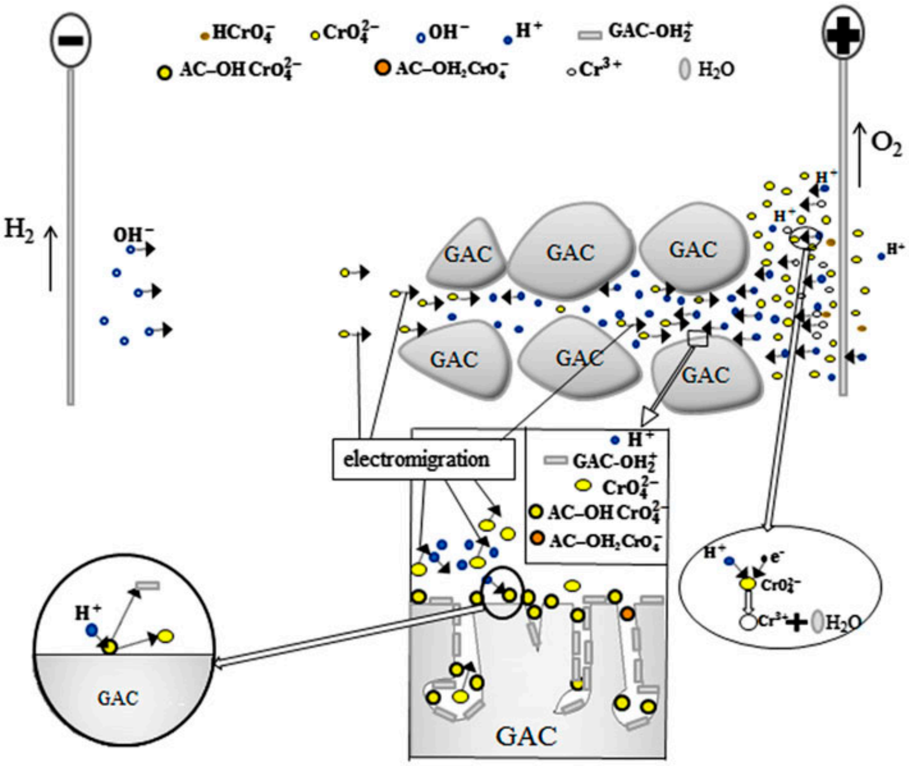

Fig. 8. Schematic diagram is summarizing regeneration processes of GAC by applying an electric current.

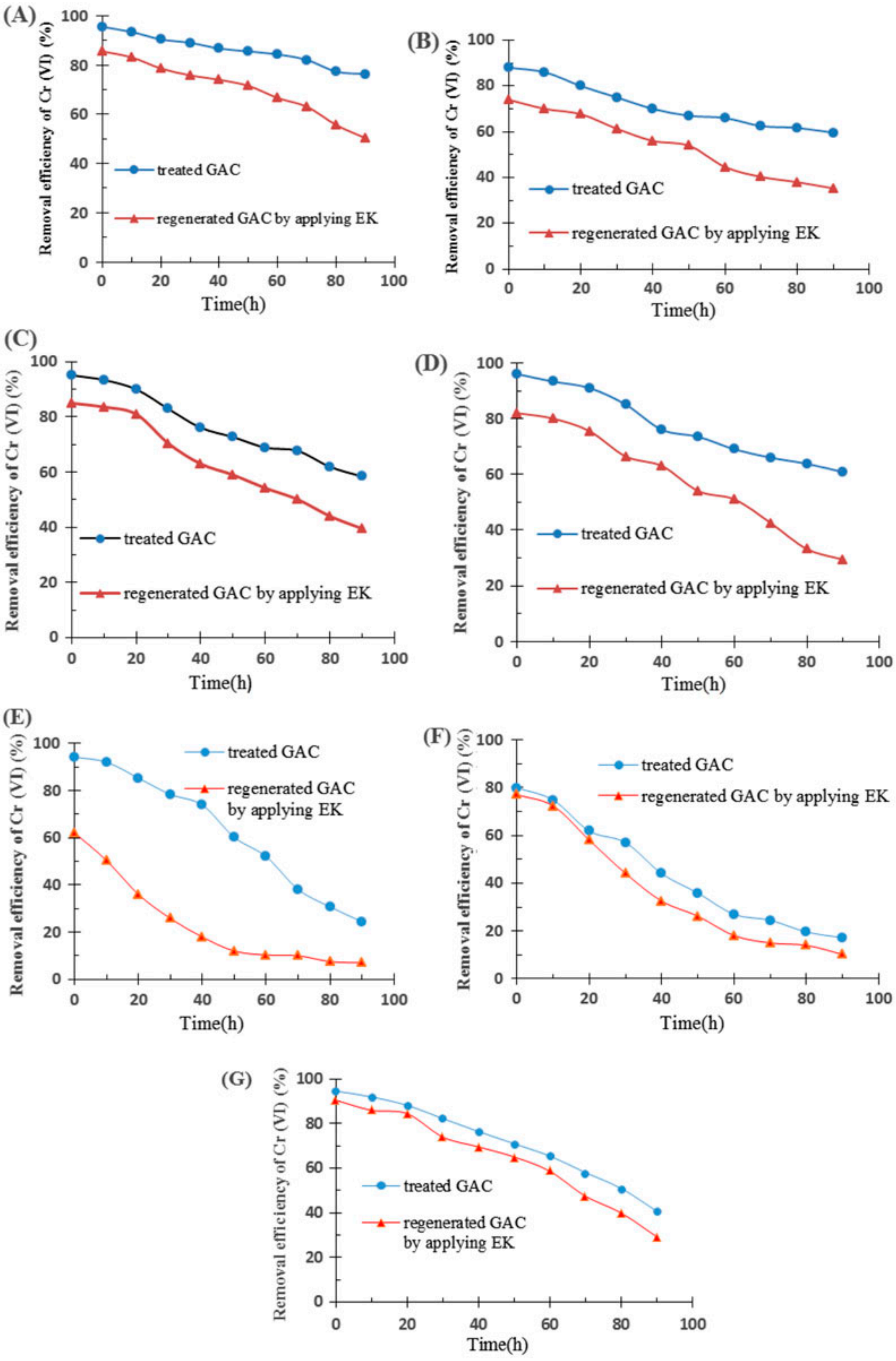

Fig. 9. Variations of the percentage of the removal of Cr(VI) by PRB with (acid treated granular activated carbon (GAC) and regenerated (GAC) by applying EK) with the time (time applying EK = 8 h), A: test (1), B: test (2), C: test (3), D: test (4), E: test (5), F: test (6), and G: test (7).

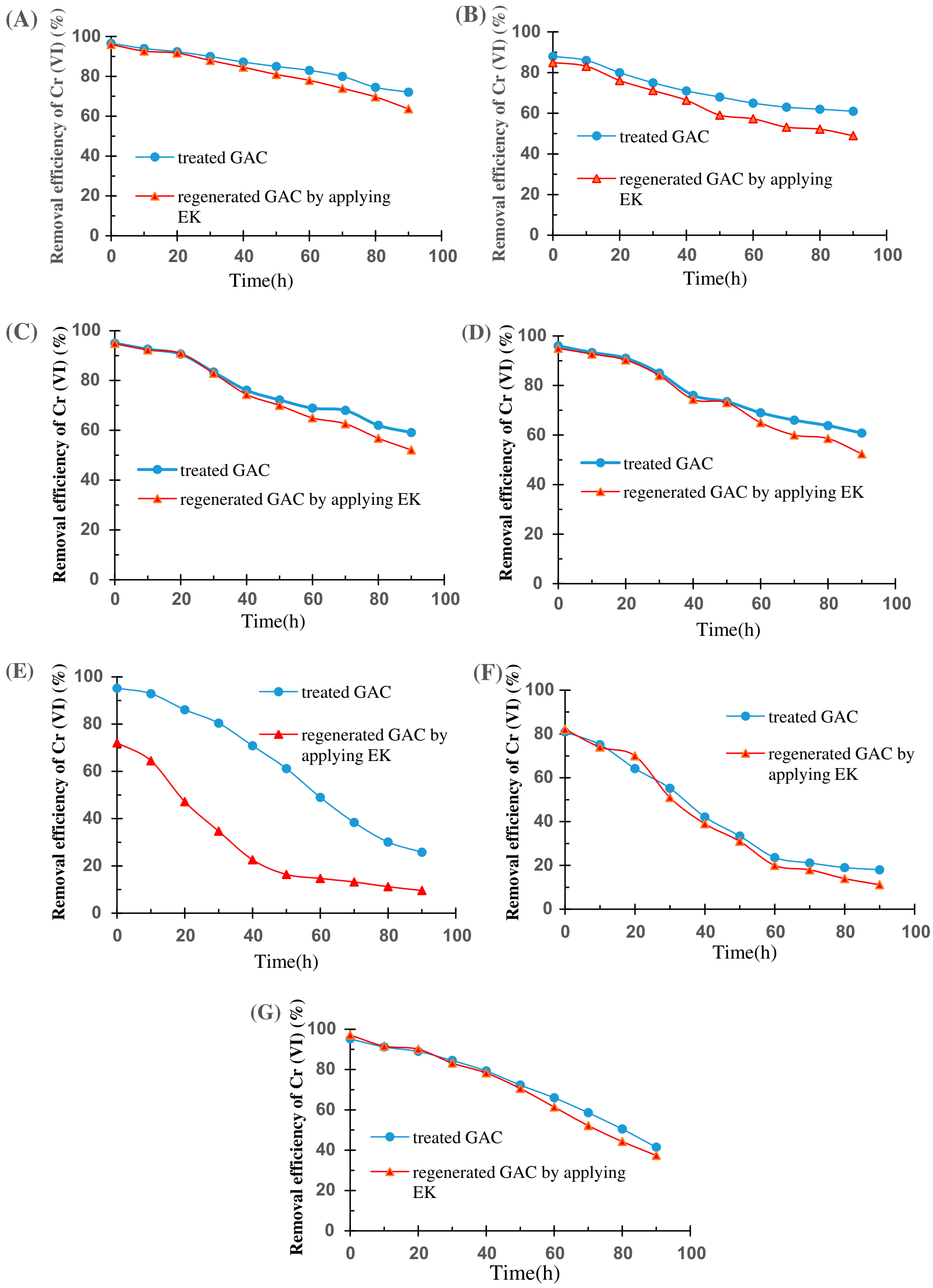

Fig. 10. Variations of the percentage of the removal of Cr(VI) by PRB with (acid treated granular activated carbon (GAC) and regenerated (GAC) by applying EK) with the time (time applying EK = 24 h), A: test (1), B: test (2), C: test (3), D: test (4), E: test (5), F: test (6), and G: test (7).

They are, however, only moderately oxidizing at high pH [25]:

$$CrO_4^{2-} + 4H_2O + 3e^- \rightarrow Cr(OH)_3 + 5OH^- \quad (9)$$

So it was found that the concentration of Cr(III) became less in the anode reservoirs after applying an electrical current when the initial pH was high. For example at test 5 (pH 8) the initial concentrations of Cr(VI) and Cr(III) in the anode reservoir before applying an electrical current were 19 and about 0 mg L^{-1}, respectively while after applying an electrical current for 24 h, the pre-mentioned initial concentrations became 20.2 and 4.1 mg L^{-1}, respectively. At this test the concentrations of Cr(VI) and Cr(III) after PRB at time = 90 h (in the cathode reservoir) before applying an electric current were 14.5 and about 0 mg L^{-1}, respectively whereas after applying an electrical current for 24 h Cr(VI) concentration became 1.64 mg L^{-1} and Cr(III) was negligible.

All tests lasted 90 h in which the simulated polluted groundwater was prepared from the stock solution, using deionized water with a Cr(VI). The pH solution had various values of 4.5, 5.5, 6.5, and 8 while the initial Cr(VI) concentration had the values 12, 19, 26, and 33 mg L^{-1} as it was shown in Table 3. This solution had been supplied to the inter compartment, and the effluent samples were collected at an exit compartment at the appropriate interval and analyzed for Cr(VI) concentration. It can be found that high rates of Cr(VI) removal are observed within the first time interval, the average efficiency of the removal of Cr(VI) between $t = 0$ and $t = 50$ h is ranging from 75 to 90% according to the values of the parameters used in this tests and then over time the removal of Cr(VI) decreases to about (65–80%). Thus, after 90 h the PRB layer becomes almost inefficient, therefore EK was applied for 8 h but it was clear that the energy applied was not enough for a complete regeneration Fig. 9. However, this can be improved by prolonging the treatment periods. So EK was applied on the layer of PRB for 24 h, here we noted that it restored a large part of the efficiency to remove Cr(VI). Within the first time interval, the average efficiency of the removal of Cr(VI) between $t = 0$ and $t = 50$ h was restored to about (55–85%), then over time the efficiency to remove Cr(VI) decreases to about (48–73%), Fig. 10. This means we need to apply EK at least 24 h in this tests to restore a large part of the PRB layer's efficiency to adsorb Cr(VI).

6. Conclusions

The studies showed that the GAC can be used as a good adsorbent for the removal of Cr(VI) from aqueous solution and the adsorption of Cr(VI) was more effective in the case of acid-treated GACs, resulting in increased acidic functional groups, but over time adsorption of Cr(VI) decreased. So this study included applying the EK for regeneration of acid treated activated carbons in PRB layer.

The GAC was successfully regenerated by using the EK under potential gradient of 5 V cm^{-1}, current electric 30–50 mA and a time elapse of 24 h.

It was clear that energy applied was not enough for the completion of regeneration if the elapsed time of treatment 8 h and we can improve this by prolonging the treatment periods.

Acknowledgments

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Symbols

C_0	—	initial Cr(VI) concentrations (mg L^{-1})
C	—	final Cr(VI) concentrations (mg L^{-1})
LOI	—	loss on ignition

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