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Removal of 2-chlorophenol from aqueous solutions using activated carbon-impregnated Fe(III)

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ABSTRACT

This manuscript combines both the advantages of the high surface area of activated carbon (AC) and the strong high affinity of Fe(III) for reacting with phenolic compounds. So, AC, activated carbon-impregnated Fe(III) (AC-Fe), activated carbon-immobilized Eriochrome Blue Black as a complexing agent (AC-EBB) and its impregnated Fe(III) form (AC-EBB-Fe) were prepared and characterized using Fourier transform infrared spectroscopy and Scanning electron microscope. Batch experiments were conducted at 25°C, at pH values 3, 6, 9, and 12, with 50 mg/L 2-Chlorophenol (2-CP) concentration, 25 mg adsorbent mass and a 1 h shaking time to evaluate and compare their efficiency for the removal of 2-CP. Generally, the impregnated Fe(III) adsorbents were better than the non impregnated ones. Moreover, AC-Fe adsorbent was the best according to the order AC-Fe (97.0%) > AC (89.9%) > AC-EBB-Fe (79.0%) > AC-EBB (65.9%) judging from values of percentage extraction at pH 9. So, the optimization of 2-CP removal using AC-Fe was thus continued at different parameters, including pH, initial 2-CP concentration, and shaking time. The equilibrium data in aqueous solution were well fitted with Langmuir sorption isotherm (Q_o 333.3 mg/g, R^2 0.975) In addition, kinetics of 2-CP adsorption onto AC-Fe followed a pseudo-second-order reaction. Application of AC-Fe for the removal of 2-CP from natural water samples was achieved successfully.

Keywords: Iron; Activated carbon; 2-Chlorophenol; Eriochrome Blue Black; Natural water samples

1. Introduction

Phenol and its derivatives are one of the most common environmental contaminants. The Phenolic derivatives are largely used as intermediates in the production of plastics, colors, pesticides, insecticides, etc. Phenols cause unacceptable taste and odor of drinking water and can exert negative effects on different biological processes [1,2]. In this context, chlorophenols (CPs) may be produced when wastewater or drinking water is disinfected with chlorine. They are also produced during the bleaching of wood pulp with chlorine in paper manufacturing. Moreover, animals that were given food or drinking water containing CPs at high levels developed negative health effects. The major effects of CPs were on the liver and the immune system [3].

So, different methods have been utilized for removing phenols from aqueous solutions. These

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methods include, reverse osmosis [4], physicochemical [5], solvent extraction [6], photocatalytic degradation [7], and adsorptive solid phase extraction (SPE) technique. SPE has become a powerful tool for the separation of various inorganic and organic analytes [8,9] due to its simplicity, flexibility, economic, rapid [10,11], and environmentally benign, especially in case of using adsorbents of natural origin [9].

In fact, various types of adsorbents have been studied for the removal of phenol and its chloro derivatives. Thus, multiwalled carbon nanotubes [12] and coal fly ash were used for the removal of phenol [13]. Amberlite XAD-16 [14] and surfactant-modified zeolite [15] were used for the removal of phenol and 4-CP. Cibacron blue F3GA-carrying poly(2-hydroxyethylmethacrylate) microbead as dye-affinity adsorbent was used to remove 3-CP, 4-CP, and 2,4,6-tri CP [16]. Hypersol–macronet resin was adapted for the removal of 2-CP, 3-CP, and 4-CP [17]. However, activated carbon (AC) is still, by far, the most important adsorbent used currently in the environmental pollution control due to its large surface area and high adsorption capacity [18–20]. Although advanced technologies devoted for CPs removal are now in continuous progress [21], modification of AC to maximize its applications for water treatment is still attractive [22]. There are several reports on the use of different types of AC for the removal of phenol and its chloro-derivatives. For instance, AC from rattan saw dust was used to remove 4-CP [1], and AC from agricultural waste was used to remove 2,4-diCP [23], and this from coconut shell was used to remove 4-CP and 2,4,6-triCP [24]. Moreover, AC modified by hydrochloric acid [25], and this from paper mill sludge [26], in addition to, AC prepared from corncobs [27] was adapted for phenol removal. Generally, utilization of low cost, biomass, carbonaceous, and nonconventional adsorbents for the removal of phenol and its derivatives was recently reviewed [28,29].

The main objective of this manuscript is to assess the potentiality of AC adsorbents-impregnated Fe(III), activated carbon-impregnated Fe(III) (AC-Fe), and activated carbon-immobilized Eriochrome Blue Black (AC-EBB-Fe) for the removal of 2-CP from aqueous solutions compared with the non impregnated, AC and AC-EBB. The study was thus planned to be continued to optimize, discuss the adsorption process, and kinetics for the adsorbent exhibits the highest potential.

2. Experimental

2.1. Instruments

Perkin-Elmer 100 series (Beaconsfield, Bucks, UK) was used to obtain Fourier transform infrared (FT-IR) spectra for AC and its modified forms. FEI Scanning electron microscope (SEM) Quanta FEG 450 was used to obtain SEM for AC and AC-Fe. Surface characterization of AC was performed using Quantachrome Autosorb 1. UV/vis spectrophotometer (MultiSpec-1501; Shimadzu) was used for spectrophotometric analysis of 2-CP solutions. pH meter Jenway 3505 was used for pH measurements.

2.2. Chemicals and solutions

All chemicals used were of analytical reagent grade. 2-CP and AC were purchased from Fluka. Eriochrome blue-black B [1-(1-hydroxy-2-naphthylazo)-2-naphthol-4-sulfonic acid sodium salt], hydrochloric acid and sodium hydroxide were obtained from Merck Ltd. Ferric nitrate [$Fe(NO_3)_3{\cdot}9H_2O$] and nitric acid were purchased from (BDH, Poole, England). Stock solution of 2-CP (1,000 mg/L) was prepared by using doubly distilled water (DDW) stored in a brown glass bottle to avoid photo-oxidation. The test solutions (50–700 mg/L) were prepared by diluting the stock solution to the desired concentration. The pH was adjusted to the required value using 0.1 N HCl and 0.1 N NaOH.

2.3. Maximum absorbance and calibration curve

The initial and final 2-CP concentrations were determined spectrophotometrically. Maximum absorption was measured at 273 nm for pH 3–9, and at 293 nm for pH 12 due to shift in maximum absorbance. Standard calibration curve for 2-CP was linear ($r^2 = 0.998$) in the concentrations range 1–160 mg/L. The concentrated solutions were diluted to fall within this range.

2.4. Modification of AC

2.4.1. Acid-treated AC

AC was treated by keeping it in 10% (v/v) HCl solution for 24 h [25]. Then it was filtered and washed thoroughly with DDW to neutral and dried in an oven for 6 h at 100°C. The main surface characteristics of this adsorbent is determined to be: BET surface area 1,149 m^2/g, pore volume 0.52 cm^3/g, and an average pore diameter 1.8 nm.

2.4.2. Activated carbon-impregnated Fe(III)

AC-Fe was obtained by magnetic stirring of 2 g AC with iron (III) solution (3.615 g $Fe(NO_3)_3{\cdot}9H_2O$ dissolved in 500 ml 0.25 M nitric acid) for 3 h at room temperature. The adsorbent thus produced was filtered and washed thoroughly with DDW, then dried in an oven for 6 h at 100˚C.

2.4.3. Activated carbon-modified Eriochrom Blue Black

It was synthesized by the impregnation of 5 g of AC with 0.225 g EBB dissolved in 1 L DDW for 72 h at room temperature. The mixture was then filtered and the adsorbent produced was washed thoroughly with DDW till the filtrate became colorless to ascertain that it gets rid of the nonimmobilized Eriochrom Blue Black. AC-EBB was then dried in an oven for 6 h at 100˚C.

2.4.4. Activated carbon-modified Eriochrom Blue Black-impregnated Fe(III)

AC-EBB-Fe was synthesized by magnetic stirring of 2 g of AC-EBB with Fe(III) solution for 3 h at room temperature. The product was filtered, washed, and dried as before.

2.5. Surface coverage determination

The surface coverage is the concentration of Fe(III) incorporated in AC-Fe and AC-EBB-Fe adsorbents in mg/g. It was determined by subtracting the concentration of Fe(III) remained in the filtrate after the impregnation process (batch mode) from its initial concentration divided by the mass of the adsorbent. On the other hand, the concentration of EBB-impregnated AC to give the adsorbent AC-EEB was determined using thermal desorption method [30]. According to this method, 100 mg sample of AC-EBB was weighed in a dry porcelain crucible and put in a muffle furnace. The temperature was gradually increased to 500˚C and the ignition was completed at this temperature for 1 h. The remaining AC was left to cool and weighed to determine the desorbed EBB by weight difference. A Blank sample of AC was subjected to the same thermal desorption procedure as described, for comparison.

2.6. Batch method for 2-CP adsorption

The adsorption experiments were carried out in a batch mode by adding 25 mg of each of modified-AC adsorbents to 25 mL of 2-CP solution at known concentration (50–700 mg/L) and at the pH values 3, 6 (natural), 9, and 12. The mixtures were shaking in 50 ml volumetric flask for 1 h at room temperature to attain equilibrium. The selection of contact time was based on preliminary studies which indicated that 1 h contact time was adequate for the equilibration of 2-CP adsorption on modified ACs. After filtration, the final concentration of 2-CP in the filtrate was measured spectrophotometrically.

The percentage adsorption (% *E*) and adsorption capacity (Q_m) of 2-CP was calculated according to the following equations:

$$\% E = (C_0 - C_e)/C_0 \times 100 \tag{1}$$

$$Q_m = (C_0 - C_e) \times V/m \tag{2}$$

where C_0 and C_e are the initial and equilibrium concentrations of 2-CP in mg/L, respectively, m is the mass of adsorbent in g, and *V* is the volume of solution in L.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy

The FT-IR spectra of the four adsorbents are presented in Fig. 1. AC showed three significant stretching vibration bands at 1,192.44, 1,578.80, and at 3,380.66 cm^{-1}. The first band can be attributed to the C–C and C–O in acids, alcohols, and phenols groups [31], the second band was assigned to C=C of aromatic rings, while the third band was assigned to O–H of alcohol and phenol groups [32]. The new peak at 1,044 cm^{-1} in AC-EBB was argued to S–O stretching in sulfonate group [33,34], present in EBB. However, stretching bands due azo- and phenolic-hydroxyl groups incorporated EBB could not be distinguished because they were overlapped with stretching bands of aromatic C=C and phenol groups attributed to AC.

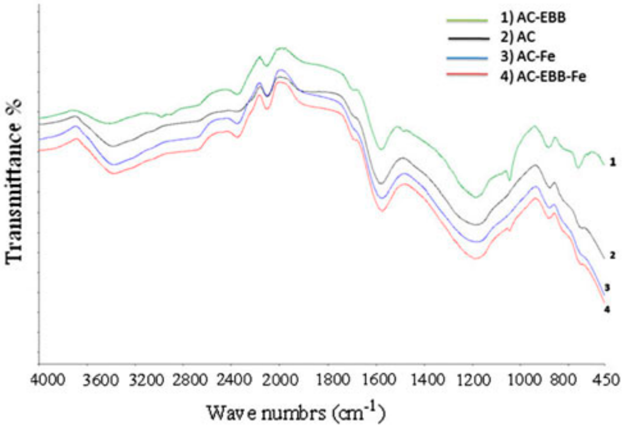

Fig. 1. FT-IR spectra for the adsorbents: (1) AC-EBB, (2) AC, (3) AC-Fe, and (4) AC-EBB-Fe.

3.2. Surface coverage

The concentration of Fe(III) impregnated AC and AC-EBB yielding AC-Fe and AC-EBB-Fe adsorbents was evaluated to be 63.4, and 131.9 mg/g. These values showed that the impregnation of EBB as a complexing agent on AC surface greatly increased Fe(III) uptake. It was suggested that the iron ions were fixed to AC and AC-EBB through the interaction and binding to AC acidic groups- and coordinating groups- incorporated EBB. On the other hand, the concentration of EBB-impregnated AC to give the adsorbent AC-EEB was determined to be 40 mg/g based on thermal desorption method [30].

3.3. Scanning electron microscope

SEM is a well-known tool for studying surface morphology of the materials. Fig. 2 illustrates the SEM images (magnification = 1600×) for AC before and after Fe(III) impregnation (AC-Fe). The SEM image for AC showed smooth surfaces with long linear ridges along with rough surfaces with undistinguished shapes. After Fe(III) impregnation, AC-Fe showed accumulation of the adsorbate on both smooth and rough surfaces of AC. Combining the above characterization data, it was revealed that the modification process for AC was successful.

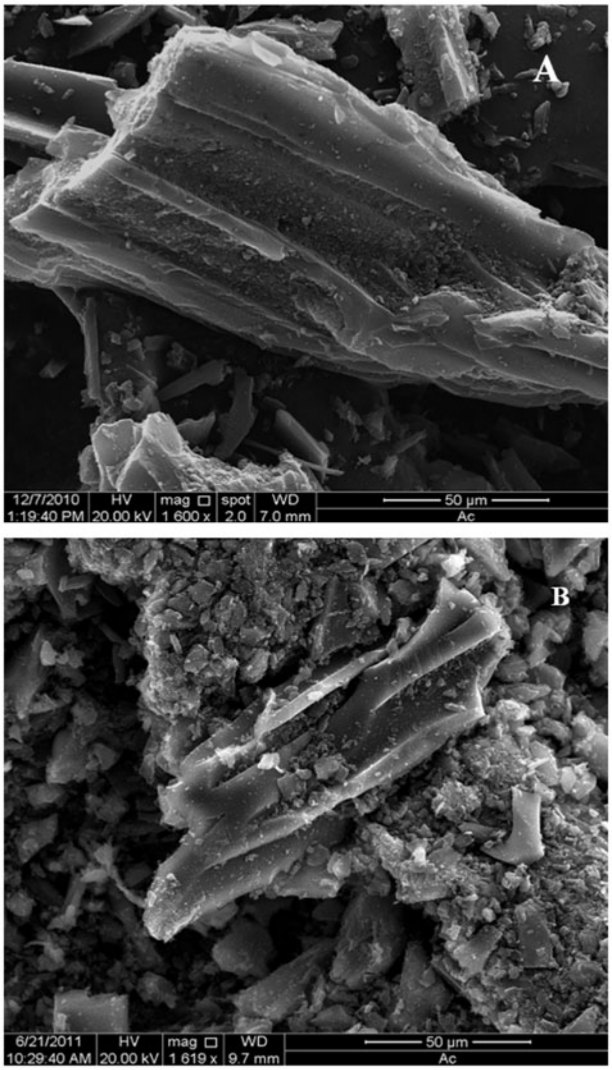

Fig. 2. SEM images for AC (A) and AC-Fe (B).

3.4. Effect of solution pH

The effect of pH on the adsorption process is an important factor. It determines the charge of the adsorbent and the degree of ionization of the adsorbate. The isoelectric point (IEP) values for plain AC were between 3.9 and 4.9 depending on the ionic strengths [35]. So, its surface charge was found to be positive at pH < IEP and negative at pH > IEP. On other hand, 2-CP is a weak acid with a pKa value equal to 8.55 [36]. At pH < pKa, it is present in aqueous medium as an undissociated molecular form, while it begins to partially dissociate at pH > pKa to reach complete dissociate at pH 11 [1,37].

In order to examine the efficiency of the modified-AC adsorbents as a function of pH, batch experiments were carried out at four different pH values (3, 6, 9, and 12). The other parameters, including initial 2-CP concentration (50 mg/L), shaking time (1 h), and temperature (25˚C) were maintained constant during the experiments. The results, as illustrated in Fig. 3, show high percentage extraction values of 2-CP onto the four adsorbents, especially at pH 9 according to the order AC-Fe (97.0%) > AC (89.9) > AC-EBB-Fe (79.0%) > AC-EBB (65.9%). This order corresponds to the adsorption capacity values 48.5, 44.9, 39.5, and 32.9 mg/g. On the other hand, at higher pH values, there was a remarkable decrease in the removal efficiency until it completely diminished at pH 12. This can be explained on the basis that at pH > pKa of 2-CP, there is a gradual increase in the strength of the repulsion between the negatively charged surface of the adsorbents and the dissociated 2-CP molecules, in addition to its anion–anion repulsion originating in the medium [38]. However, the situation is different at pH < pKa for 2-CP, where this region includes moderately acidic or basic (pH 7 ± 1) to the strongly acidic one. So, the adsorption of 2-CP in this case does not occur due to electrostatic interaction or columbic forces, but due to specific π–π interaction between the 2-CP aromatic ring and similar rings of the carbon surface [39]. In fact, the mechanism for 2-CP removal

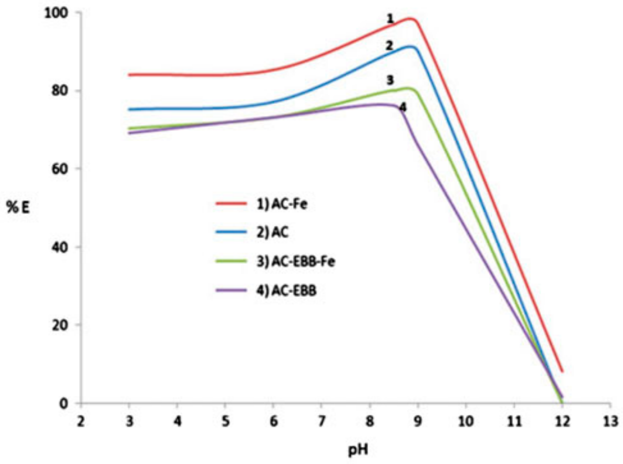

Fig. 3. Effect of solution pH on 2-CP removal onto the different adsorbents ($C_0 = 50$ mg/L, $T = 25$℃, shaking time = 1 h, adsorbent mass = 25 mg).

using Fe(III)-impregnated AC is suggested to be a combination of the adsorption capacity of AC and the amount of iron ions bound to AC where they act as attracting centers for interaction with 2-CP phenol, either as an undissociated or dissociated species depending on the pH.

Based on the results of extraction percentages, the work was continued to optimize AC-Fe adsorbent for the removal of 2-CP from aqueous solution because it exhibited the highest efficiency. In this context, it is important to denote that although the concentration of 2-CP was relatively low (50 mg/L), it was enough to differentiate between the removal performance of the four adsorbents.

3.5. Effect of initial 2-CP concentration on adsorption capacity and sorption isotherms

Studying the effect of initial 2-CP concentration (50–700 mg/L) on its adsorption onto AC-Fe as a function of pH revealed that AC-Fe exerts more or less the same capability for adsorption of 2-CP along the pHs used. For instance, the adsorption capacity was determined to be 81.47, 83.59, and 83.31 mg/g at pH values 3, 6, and 9, respectively at 100 mg/L initial 2-CP concentration. These values increased to 222.7, 208.84, and 229.99 at 400 mg/L initial 2-CP concentration and reached maximum values of 317.89, 275.67, and 280.55 mg/g at 700 mg/L initial 2-CP concentration in the same order of pH values studied. These results denote to the high affinity of AC-Fe for binding to 2-CP [40] present as an undissociated or dissociated form, either in acidic or basic medium, respectively [1,37].

Sorption isotherms are usually determined under equilibrium conditions. They indicate how the adsorbents molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. Fitting the data to different isotherm models is an important step to find a suitable model that can be used for the performance of adsorption process. The most frequently employed models are Langmuir and Freundlich.

The adsorption isotherms for binding of 2-CP with Fe-AC were determined by the batch technique at pH values 3, 6, and 9.

The linear form of Langmuir's isotherm [41] model is given by Eq. (3):

$$C_e/q_e = C_e/Q_0 + 1/bQ_0 \tag{3}$$

where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent; Q_0 and b are Langmuir constants related to adsorption capacity and the adsorption equilibrium constant, respectively. For the Langmuir isotherm, when C_e/q_e is plotted against C_e at the pH values 3, 6, and 9, a straight line with a slope of $1/Q_0$ is obtained as shown in Fig. 4. The correlation coefficients, R^2 indicated that the adsorption data of 2-CP on AC-Fe are well fitted to the Langmuir isotherm at the studied pH values supporting the formation of monolayer coverage of 2-CP molecules at the surface of AC-Fe. The Langmuir constants b and Q_0 were calculated from Eq. (3) and are listed in Table 1. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless

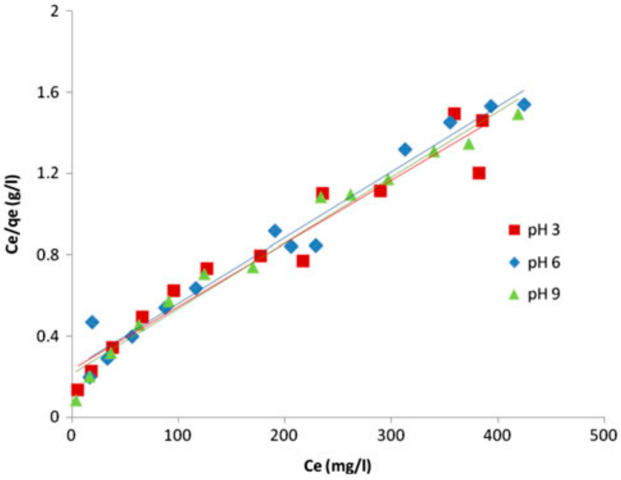

Fig. 4. Langmuir sorption isotherm of 2-CP onto AC-Fe at different pH values ($T = 25$℃ shaking time = 1 h, adsorbent mass = 25 mg).

Table 1
Langmuir constants and correlation coefficients for adsorption of 2-CP onto AC-Fe as a function of pH

pH	Langmuir constants		R^2
	Q_o mg/g	b L/mg	
3	333.33	0.0128	0.937
6	333.33	0.0126	0.970
9	333.33	0.0142	0.975

equilibrium parameter (R_L) [42]. The parameter is defined by:

$$R_L = 1/(1 + bC_0)$$

where b is the Langmuir constant and C_0 (mg/L) is the highest initial 2-CP concentration. The parameter R_L indicates the shape of isotherm as follows: $R_L > 1$ unfavorable, $R_L = 1$ linear, $0 < R_L < 1$ favorable and $R_L = 0$ irreversible. It was found for the 2-CP concentrations studied (50–700 mg/L), the R_L values were in the range (0.61–0.10), (0.61–0.10) and (0.58–0.09) at pH 3, 6, and 9, respectively. These values of R_L indicate that the adsorption process is favorable for 2-CP concentrations and at respective pH values as well (1000 mg/L).

The linear form of Freundlich isotherm [43] is given by the Eq. (4):

$$\log q_e = \log k_f + 1/n \log C_e \tag{4}$$

where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent, and k_f (mg/g (L/mg)$^{1/n}$) and n are Freundlich constants. The plot of log q_e vs. log C_e gave a straight line with slope of $1/n$, whereas k_f was calculated from the intercept value. The values of $1/n$ were found to be higher than unity (1.87–2.56) in the pH range 3–9 indicating that the adsorption of 2-CP onto AC-Fe is not obeying Freundlich model [43].

3.6. Kinetic studies

3.6.1. Pseudo-second-order

The pseudo-second-order equation [44] is expressed as:

$$t/q_t = 1/q_t^2 k_2 + 1/q_e t \tag{5}$$

where q_e and q_t are the adsorption capacities (mg/g) at equilibrium and at time t, respectively and k_2 (g/mg min) is the rate constant of pseudo-second-order sorption. By plotting t/q_t vs. t, q_e and k_2 can be determined from slope and intercept. The linear plot of t/q_t vs. t at 25°C, 50 mg/L initial 2-CP and at pH 6 shown in Fig. 5 yielded R^2 value equal to 0.999. The q_e and k_2 values were determined from slope and intercept to be 41.66 mg/g and 0.075 (g/mg min), respectively. Moreover, there is a good agreement between the experimental adsorption capacity, 40.86 mg/g and the calculated one, 41.66 mg/g at 50 mg/L initial 2-CP concentration indicating the applicability of this model to describe the kinetics of the adsorption process of 2-CP onto AC-Fe.

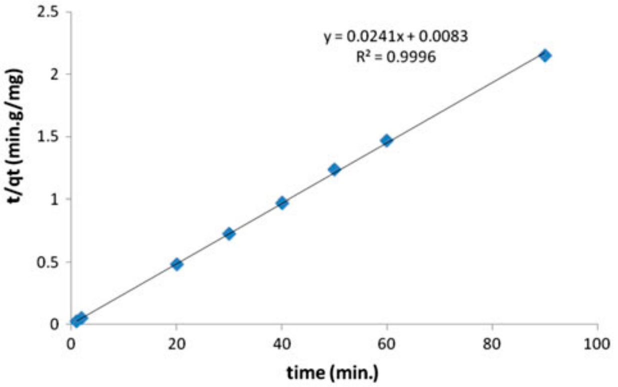

Fig. 5. Pesudo-second-order kinetics for adsorption of 2-CP onto AC-Fe (C_0 = 50 mg/L, T = 25°C, adsorbent mass = 25 mg, pH 6).

3.7. Applications

The new proposed adsorbent AC-Fe was applied for the removal of 2-CP spiked natural water samples (25 mg/L). The samples were collected from Jeddah City, KSA of Red Sea coast and ground water, and wastewater treatment station at King Abdulaziz University and tap water from our research laboratory. The quantitative recovery obtained (>98%) under batch conditions (25 mg of AC-Fe, shaking time 1 h and at natural pH) support the validity of the new adsorbent for applications with no competitive effect from other coexisting adsorbants.

3.8. Comparison with other ACs

The values of adsorption capacities and equilibrium time for a number of ACs reported in the literature for the removal of 2-CP are compiled in Table 2. It is obvious that the new adsorbent is

Table 2
Comparison of adsorption capacities and equilibrium time for a number of ACs used for 2-CP removal

Adsorbent	Adsorption capacity (mg/g)	Equilibrium time	References
Powdered AC produced by chemical activation method	140.8	1 day	[45]
Powdered AC produced by thermal activation method	250	7 days	
Granular AC produced by chemical activation method	256.4	1 day	
Granular AC produced by thermal activation method	270.3	7 days	
Four different types of AC		1 h	[46]
Dried activated sludge	239.1	1 day	[37]
Fly ash	90	1 day	
Granular AC	350.1	1 day	
AC-Fe	317.89 at pH 3, 275.67 at pH 6, and 280.55 at pH 9	1 h	This work

characterized by high adsorption capacity and fast kinetics.

4. Conclusion

Generally, it was found that the efficiency of AC-impregnated Fe(III) adsorbents for the removal of 2-CP was higher than the nonimpregnated ones. Moreover, AC-Fe was the highest according to the order, AC-Fe > AC > AC-EBB-Fe > AC-EBB. Furthermore, the ability of AC-Fe for removing 2-CP from aqueous solutions is possible along a wide range of pH 3–9. These phenomena depicting the high affinity of Fe(III)-incorporated adsorbent for binding to 2-CP present as undissociated or partially dissociated forms. In short, AC-Fe adsorbent combines both the advantages of the surface characteristics of AC (BET surface area 1,149 m^2/g, pore volume 0.52 cm^3/g, and an average pore diameter 1.8 nm where no significant decrease or very similar surface area is expected for AC-Fe [31]) and the pronounced capability of Fe(III) for reacting with phenolic compounds. This reflected in high adsorption capacity along with fast kinetics.

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