
Synthesis of a high characteristics activated carbon from walnut shell for the removal of Cr (VI) and Fe (II) from aqueous solution: single and binary solutes adsorption

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Abstract

A high performance activated carbon was synthesized using walnut shell as a solid waste through a two-step zinc chloride chemical activation-thermal pyrolysis process. Characterization results demonstrated its porous structure with very good textural properties such as high BET surface area (1223 m²/g) and high total pore volume (0.85 cm³/g). The final adsorbent was used for adsorption of Fe (II) and Cr (VI) from aqueous solution. Effect of pH, initial concentration of metal ions, temperature, and contact time on adsorption capacity of the adsorbent was investigated. Adsorption results revealed that the maximum removal of Fe (II) and Cr (VI) ions, occurred at pH 4.5 and 2 respectively, were 96.2% and 99% at 313K. The equilibrium and kinetics data for adsorption of single-component ions were well described by the Sips isotherm and the pseudo-nth-order models, respectively. The impact of competing ions was studied by adsorption of a binary solution of Fe (II) and Cr (VI) ions. The binary adsorption isotherm was described by the modified Langmuir model and model parameters were found following an optimization procedure by genetic algorithm. Finally, the developed walnut-shell based activated carbon showed higher adsorption efficiency compared to other activated carbons at similar conditions.

Keyword: Heavy Metal, Adsorption, Activated Carbon, Walnut Shell, Isotherm

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1. Introduction

Water pollution is a major global problem which requires ongoing research and revision of water resource policy at all levels. Protecting water sources is essential to ensure human health. Every year at least five million people die from water-related diseases worldwide. Preventing pollutants from entering water sources is an effective way to ensure clean drinking water and thus prevent human sickness. Hence, it is important to know whether common water treatment methods can effectively remove toxic chemicals.

Among all water pollutants, heavy metals are an important category which should never be neglected. They are elements having atomic weights greater than 50 g and a specific gravity greater than 5.0 [1]. At least 20 metals are classified as harmful, and half of these are discharged into the environment in quantities that threatens human health [2]. Among the heavy metals, chromium and iron can be noted. These metals are generated from many industrial processes such as leather tanning, electroplating, mining and refining, etc. [3-5]. The presence of these metals beyond the tolerance limit in water can cause various diseases such as cancer in the gastrointestinal tract and lungs, qualm, severe diarrhea, and bleeding also kidney and gastric damage, etc. [6,7].

Several processes are available for removing heavy metal ions from wastewater including precipitation, bioremediation, ion exchange, electrochemical, membrane filtration and adsorption [8,9]. However, most of these technologies are very expensive and ineffective in reducing metal

ion rate in wastewater to permissible concentrations [9,10]. The adsorption process is yet considered as the most widely used method for the removal of metal ions from industrial effluents due to its higher treatment efficiency and lower process costs compared with the above mentioned processes [11]. Activated carbon (AC) is a porous carbon material which has a high adsorption capacity [12,13]. It is widely used in industrial wastewater [14] and gas treatment as the adsorbent [15] due to its great specific surface area, ability to reactivate, desired pore structure, good chemical resistance, and different oxygen-containing functional groups on the surface [13]. Nowadays, AC can be produced from a large number of accessible and low-cost materials containing a high carbon content and a low inorganic content such as coconut shell [16], cherry stones [17], rice husk [18], peanut shell [19], hazelnut husks [20], walnut shell [21], etc. Typically, chemical and physical activation are alternative processes for AC preparation [21]. Physical activation is performed at higher temperatures in the presence of gases such as carbon dioxide, steam, etc. [22] whereas chemical activation is carried out by dehydrating agents and oxidants such as HNO₃, NaOH, KOH and ZnCl₂. Chemical activation has its own advantages such as leading to the higher yield, employing lower temperature and shorter activation time, which is preferred over physical activation [23].

In recent years, the study on production of new ACs replacing expensive sources of carbon has increased. Many researches have been conducted in this field that indicate the high potential of ACs for adsorption of heavy

metals such as Cr (VI) and Fe (II). In this regard, Alton, *et al.* [24] produced AC from walnut shell for the removal Cr (VI) by chemical activation with citric acid. Cr (VI) ion adsorption on prepared adsorbent was modelled by Langmuir, Freundlich and D-R isotherms. The highest Cr (VI) adsorption capacity of 31 mg/g was obtained at the optimum AC at pH 2. Acarand Malkoc [25] used Beech sawdust for preparation of AC by chemical activation using sulfuric acid. The optimum contact time was 80 min and the maximum adsorption efficiency of 100% was obtained at pH 1. This showed that the adsorption capacity of the adsorbent is strongly pH dependent. Guo *et al.* [26] investigated the uptake of Cr (VI) from aqueous solutions using AC derived from rice husk by KOH-activation and NaOH-activation under different conditions. The maximum adsorption capacity for adsorbents activated by KOH and NaOH with pH 5 and adsorbent dose of 0.8 g/L at 20°C was reported 33.7 and 33.5, respectively.

A number of attempts were also made to study the removal of Fe (II) from aqueous phase. Moghaddam *et al.* [27] used AC prepared from pomegranate peel for removing Fe (II) from aqueous solution in discontinuous operation. The investigation was carried out to find the optimum conditions including pH, contact time, the effects of initial concentration of metals ions and temperature. The kinetic data indicated that the adsorption process was controlled by pseudo-second-order equation. Also, the experimental equilibrium data were well fitted by Langmuir adsorption model, with maximum Fe (II) adsorption capacity of 18.52 mg/g at pH 6 and temperature 29°C.

Hegazi [3] could remove several metals ions (Ni^{2+} , Pb^{2+} , Cu^{2+} , Cd^{2+} and Fe^{2+}) within the concentration range of 20-60 mg/L by the AC produced from rice husk and fly ash. Also, the optimum pH required for maximum adsorption was found to be 6-7. Among these adsorbents, rice husk had the best performance for adsorption of Fe^{2+} , Ni^{2+} and Pb^{2+} whereas fly ash was effective in the removal of Cd^{2+} and Cu^{2+} .

Walnut is one of the most common agricultural products with large quantity in Iran. According to statistics, more than 270,000 tons of walnut shells are produced annually in Iran. Comprising compounds of walnut shell are hemicellulose, lignin and cellulose with a high carbon content and also some amount of extractives and ash [24] which renders it a suitable precursor for AC production. Walnut shell because of its availability as a renewable resource, good stability and high rigidity has been successfully used for AC production and its utilization in removing heavy metals by adsorption has been investigated [28,29].

The objective of the present study was to produce an AC from walnut shell with high textural properties and adsorption capacities toward heavy metals ions. The results obtained on the preparation of AC from walnut shell by chemical activation with zinc chloride and their ability to remove Cr (VI) and Fe (II) from dilute aqueous solutions are discussed. The effects of solution pH, initial metal concentration, and temperature on adsorption of these metals were studied in detail. Also, the equilibrium isotherms, kinetics, and thermodynamics of adsorption process have been studied. Besides, the multicomponent effect due to coexistence

of Cr (VI) and Fe (II) in water was investigated.

2. Materials and method

Walnut shell, for the synthesis of AC was collected from a local source in the north of Iran. All reagents used in this study were analytical grade purchased from Merck Co.,

Germany and were used without any further purification.

2-1. Preparation of activated carbons

Proximate and ultimate analyses of the walnut shell are given in Table 1.

Table 1

Proximate and ultimate analysis of walnut shell.

Parameter	Ultimate analysis (dry basis, wt%)			Proximate analysis	
	C	H	N	Humidity (dry basis, wt%)	Ash
Value	66.3	4.74	0.435	2.2	2.6

Walnut shells were firstly crushed with a high-speed rotary cutting mill and washed with distilled water several times to remove dust and other inorganic impurities, then were dried in an oven for about 24 h at 110°C and sieved to obtain particles with the size range of 0.3-0.6 mm. The powdered samples were impregnated by 0.7 M ZnCl₂ concentrated solution (98%) in the impregnation ratio of 1:2.5 (walnut shell : ZnCl₂ on dry basis) and stirred at approximately 80°C for 8 h to ensure a complete reaction between ZnCl₂ and walnut shell. Then the mixtures were filtered and the residual solids were dried at 120°C for about 48h in an oven to remove extra water. The dried impregnated walnut shell was placed in an inert atmosphere in a vertical furnace as used in our previous works [30,31] at 650°C for 1 h under the nitrogen flow of 300 mL/min at heating rate of 10°C 1/min. The resulting AC was thoroughly washed with 0.05 M hydrochloric acid and distilled water

to remove the residual ZnCl₂ and inorganic material until the pH value of the washed solution reached neutral value (pH 7). Finally, they were dried at 110°C for 24 h and were used as the adsorbent for the removal of Cr (II) and Fe (II) from water in adsorption experiments.

2-2. Characterization of the adsorbent

The textural properties of the prepared AC were determined by N₂ adsorption/desorption isotherms at 77 K in the relative pressure range of 0.01 to 0.99 using Belsorp max analyzer. Specific surface was estimated by BET method and total pore volumes were calculated in the relative pressure of ~0.99. The surface morphology of the prepared AC was examined by field emission scanning electron microscopy (FE-SEM) (VEGA II TESCAN, CZECH). Surface functional groups were identified by Fourier transform infrared spectra (FT-IR) using Spectrum RX I, Perkin-Elmer. Concentration of each metal

ion in a binary solution was measured by Varian inductively coupled plasma/optical emission spectroscopy (ICP/OES) OES-730.

2-3. Batch adsorption experiments

2-3-1. Single-component adsorption

Standard stock solution of Cr (VI) and Fe (II) (1000 mg/l) was prepared by dissolution of proper amount of $K_2Cr_2O_7$ and $FeSO_4 \cdot 7H_2O$ in distilled water. To prevent the oxidation of iron ions, a few drops of HCl solution (37 v/v%) was added to the solution and was kept in a dark glass bottle. Stock solution was then diluted to obtain the solution with desired concentration prior to adsorption experiments. Batch adsorption studies were carried out with 0.2 g sorbent per 100 mL of metal solutions at (293-313K) on a mechanical shaker with the rotation speed of 200 rpm. The initial pH of the adsorbate solution was adjusted using 0.1 N HCl or 0.1 N NaOH aqueous solution. The samples were removed from the flasks at different time intervals to check whether equilibrium was reached. After shaking, samples were filtered by the aid of a Whatman No.42 filter paper and the concentrations Cr (VI) and Fe (II) at equilibrium (C_e) were determined using a UV-vis spectrometer at wavelength of 540 and 425 nm, respectively. The amount of metal ions adsorbed q_t (mg/g) and removal efficiency R (%) by the AC were calculated according to the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

$$\%R = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

Where, C_0 , C_e and C_t (mg/L) represent concentration of metal ions in the liquid-phase at the start of the process, equilibrium

state and after t minutes, respectively. V (l) is the volume of the solution and m (g) is the mass of dry adsorbent.

2-3-2. Binary adsorption

Binary experiments for adsorption of Fe (II) and Cr (VI) were performed in similar operating conditions to single-component adsorption in terms of volume (100 mL), adsorbent mass (0.2 g per 100 mL), pH (3), stirring time (5 h) and rotation speed (200 rpm). Initial concentrations of binary metal solution was adjusted in the range of 10 to 100 (mg/L) containing 50% of each ion. The remaining concentration after start of adsorption was determined by Inductively Coupled Plasma/Optical Emission Spectroscopy.

3. Results and discussion

3-1. Characterization results

3-1-1. BET analysis

Fig. 1 indicates the nitrogen adsorption/desorption isotherms of the synthesized AC at 77K. From the figure, it is clear that as the relative pressure increases, the nitrogen uptakes increase across the whole pressure range. This adsorption behavior displays a Type IV shape isotherm according to IUPAC classification, indicating that the activated carbon is highly mesoporous [19,32]. Also, this isotherm shows an obvious increasing slope at high relative pressures ($p/p_0 > 0.8$) which can be attributed to the growth of large pores. The textural properties of the adsorbent were listed in Table 2. As the table indicates the prepared AC represents a high specific area (1223 m^2) and large total pore volume ($0.85 \text{ cm}^3/\text{g}$) which makes it susceptible for removal of heavy metal adsorption with high efficiency.

Table 2

The textural properties of the walnut shell activated carbon.

Sample	S_{BET} (m^2/g)	V_{Total} (cm^3/g)	Mean pore diameter (nm)
Walnut shell activated carbon	1223.4455	0.8465	2.7674

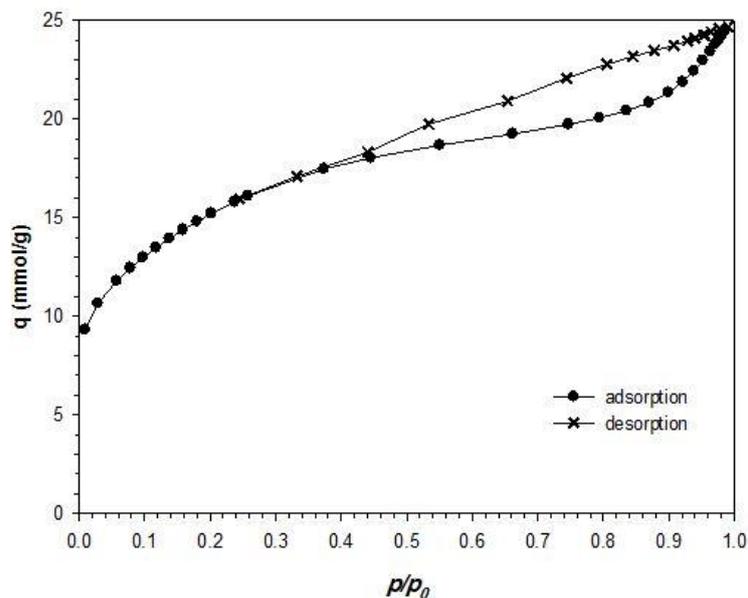


Figure 1. N_2 adsorption/desorption isotherm for activated carbon at 77 K.

3-1-2. SEM analysis

Field emission scanning electron microscopy (FE-SEM) technique was used to observe the surface physical morphology of activated carbon. Fig. 2 presents the FE-

SEM images of the activated carbons. As is indicated the prepared AC had non-uniform and porous structure with varying particle size.

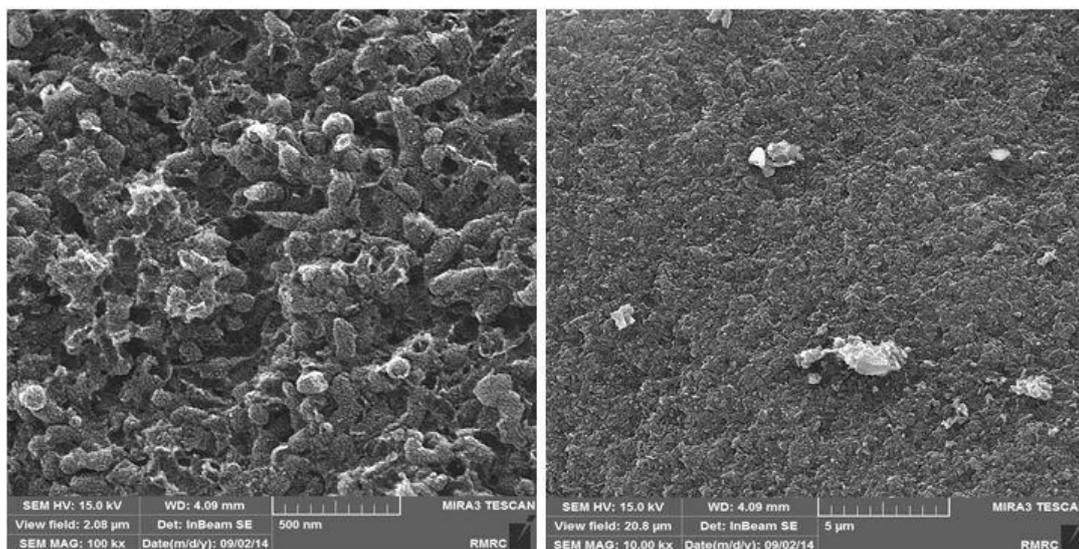


Figure 2. SEM micrographs of the activated carbon prepared from walnut shell.

3-1-3. FT-IR analysis

The adsorption capacity of an AC depends not only on its porosity but also the presence of many chemical functional groups on its surface. FT-IR spectra of the walnut shell-based AC are given in Fig. 3. Several significant peaks are observed in Fig. 3. The wide and flat band at 3200-3600 cm^{-1} can be related to the O-H stretching vibration of the surface hydroxyl groups and the presence of -NH

group [33,34]. The peaks at 2338 and 2362 cm^{-1} show the binding $\text{C}\equiv\text{C}$ groups due to symmetric or asymmetric stretching of aliphatic band that increased during carbonization [21]. The peaks at 1515 cm^{-1} and 1702 cm^{-1} correspond to aromatic groups and C=O (carbonyl) stretching vibration of the surface carbonyl respectively. The band located at about 1458 was attributed to carboxylate ion group [34,35].

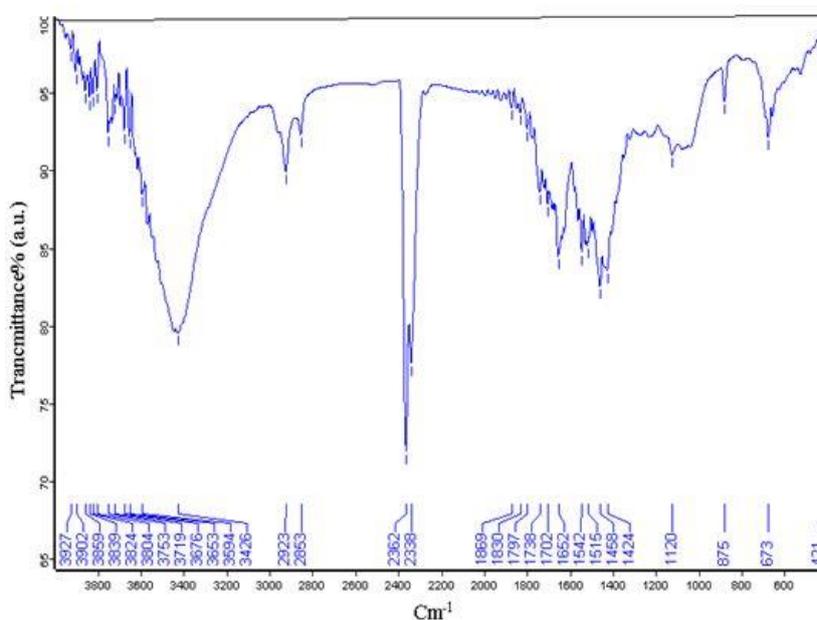


Figure 3. FT-IR analysis from activated carbon adsorbent before metallic ion adsorption.

3-2. Adsorption results

3-2-1. Effect of pH

The pH of the solution is an important parameter in the uptake of heavy metals by an adsorbent that contributes to metal ion adsorption sites on the adsorbent surface as well as chemical structure of the metal in the water. As pH increases, the charge of adsorbent surface becomes more negative, which is a good factor for adsorption of positive ions of Fe (II). But at high pH, the presence of OH^- causes precipitation of

iron ions. Therefore, in order to ensure that removal of iron ions occurs solely due to adsorption, the pH of solution was adjusted lower than precipitation pH (pH 5) according to our previous work [36]. On the contrary, as pH decreases, the charge of adsorbent surface becomes more and more positive, which provides a suitable condition for adsorption of negative ions of hexavalent chromium ($\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} , etc.). Therefore, the effect of pH on the removal efficiency of Cr (VI) and Fe (II)

by the synthesized AC was studied in the pH range of 2-6 and 2-5 respectively, while the other operational parameters including adsorbent dosage, initial ion concentration and temperature were kept constant at 2 g/L, 50 mg/L and 30°C, respectively and the results were shown in Fig. 4. It was demonstrated that removal efficiencies of Fe (II) increase from 50.6% to 92.5% by raising the initial pH of the solution to 4.5. But for Cr (VI) ions, by increasing pH of solution, removal efficiency of Cr (VI) was

reduced from 99.25% to 66.3%. The reduction in adsorption rate of Cr (VI) by increasing solution pH is attributed to accumulation of negative charge on adsorbent surface and increase of repulsiveness forces between homonymous charges [11,31]]. Thus for Cr (VI) and Fe (II) ions the maximum adsorption occurs at pH 2 and 4.5, respectively, and hence these values were chosen as the optimal pH values for further adsorption studies.

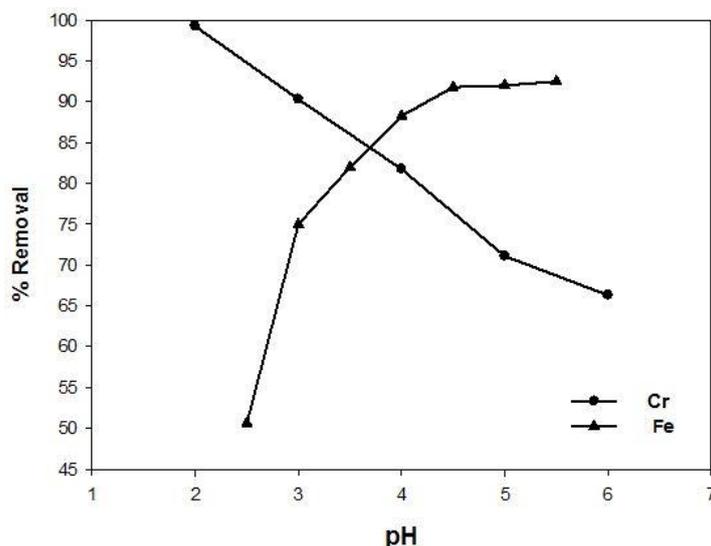


Figure 4. Effect of pH on removal efficiency of Fe (II) and Cr (VI) ions by activated carbon prepared from walnut shell ($C_0=50$ mg/L, $T=293$ K and $m=2$ g/L).

3-2-2. Effect of initial metal ion concentration

Initial concentration generates a driving force to overcome all mass transfer resistances between the aqueous phase and the solid [37]. Figure 5 shows the effect of initial concentration of metal ions on equilibrium uptake. The effect of initial concentration of Fe (II) and Cr (VI) was studied using solutions with different initial concentration in the range of 10-100 mg/L at 303 K, while keeping all other parameters

at optimum condition. According to Fig. 5, the adsorption capacity increases from 4.38 to 40.83 for Cr (VI) and 3.9 to 34.16 for Fe (II) by increasing the concentration of metal ions from 10 to 100 mg/L. In low concentrations of metal ions, most of the available active sites on adsorbent remained unsaturated and uptake capacity is low. In general, increasing the initial concentration of adsorbate leads to increasing the driving force for mass transfer and subsequently increases the adsorbent capacity [38].

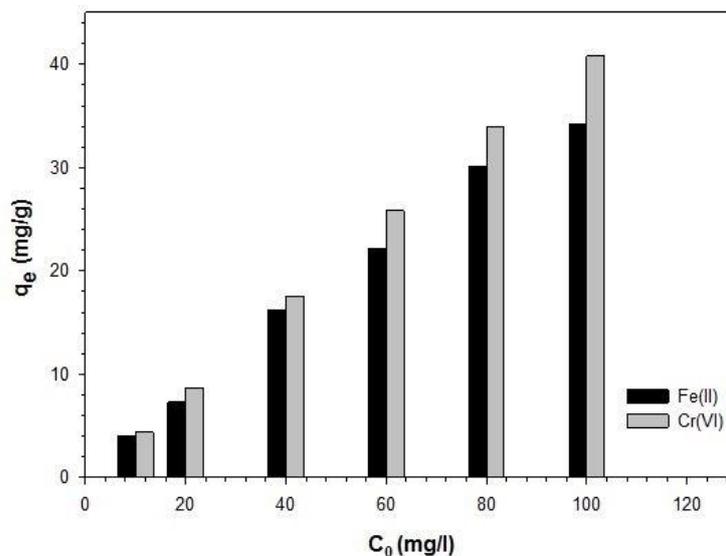


Figure 5. The effect of initial concentration of Fe (II) and Cr (VI) ions on adsorption capacity of the activated carbon ($T=303$ K and $m=2$ g/L).

3-2-3. Effect of temperature

The effect of temperature was investigated from adsorption experiments carried out at three constant temperatures, i.e. 20, 30 and 40°C that are shown for Fe (II) and Cr (VI) ions in Fig. 6. During these experiments, the other conditions were kept constant, i.e. ion

concentration of 40 mg/L, adsorbent dose of 0.2 g, pH 2 for Cr (VI) and pH 4.5 for Fe (II), respectively. The experimental data show that the adsorption capacities for both metal ions increased with an increase in temperature, indicating endothermic nature of the sorption processes.

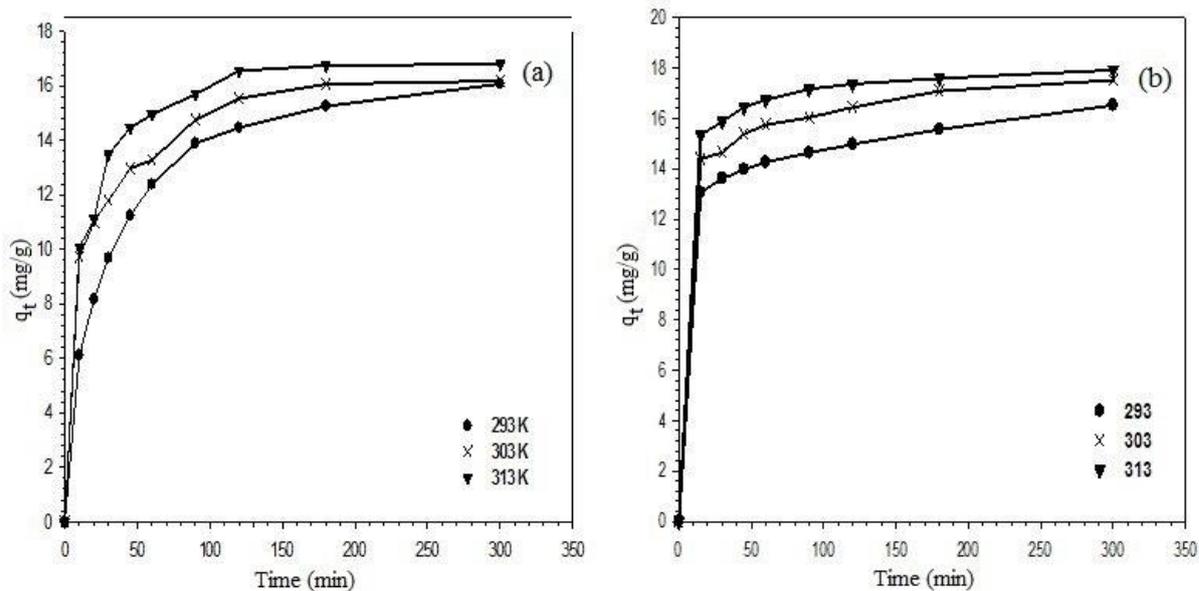


Figure 6. Fe (II) (a) and Cr (VI) (b) ions adsorption data on the walnut shell activated carbon at 293, 303 and 313 K.

3-3. Adsorption isotherm

3-3-1. Single solution

Adsorption isotherm is a relationship which connects the concentration of an adsorbate in sorbed phase to its concentration in bulk solution. In order to evaluate the sorption isotherms for the adsorption of Fe (II) and Cr (VI) ions onto the synthesized AC, adsorption equilibrium data were described by several model isotherms such as Langmuir, Freundlich and Sips. Langmuir isotherm is commonly expressed as:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (3)$$

Where q_e and q_{\max} (mg/g) are the equilibrium and the maximum adsorption capacities, respectively, K_L (l/mg) is the Langmuir equilibrium parameter for adsorption and C_e (mg/L) is the equilibrium concentration in liquid phase. This model assumes uniform energies of adsorption onto the surface and suggests that uptake occurs on a homogeneous surface by monolayer coverage with equal active sites [39]. The Freundlich isotherm is defined as the following equation:

$$q_e = K_F C_e^{1/n} \quad (4)$$

In equation (4), K_F ((mg/g)(l/mg)^{1/n}) is Freundlich constant and determines the adsorption capacity of the adsorbent, n is the dimensionless parameter which indicates density of adsorption. This model is the first known relationship describing the reversible and non-ideal adsorption

based on heterogeneous surface and can be applied to multilayer adsorption on the adsorbent surface [39]. The Sips model is given as [40]:

$$q_e = \frac{q_{\max} (K_{LF} C_e)^b}{1 + (K_{LF} C_e)^b} \quad (5)$$

Where K_{LF} (1/mg) is Sips model constant and exponent of b shows the degree of heterogeneity. Sips isotherm is a combined form of Langmuir and Freundlich statements presented for predicting the heterogeneous adsorption systems. The behavior of this model is similar to Freundlich model with the difference being that this relationship assumes a limited saturated level for absorption at high concentrations [40].

The results obtained from equilibrium adsorption of Fe (II) and Cr (VI) ions by the walnut shell-based AC are shown in Fig. 7. The values obtained for the parameters of three model isotherms along with the regression coefficients for Fe (II) and Cr (VI) are listed in Table 3. According to the results, it is clear that the Langmuir-Freundlich model fits the results slightly better than the other models. Sorption capacities from the present study were compared with other adsorbents from other studies in Table 4. As the table indicated the walnut shell-based AC developed in this study has shown superior adsorption capacity at similar conditions owing to the better textural properties.

Synthesis of a high characteristics activated carbon from walnut shell for the removal of Cr (VI) and Fe (II) from aqueous solution: single and binary solutes adsorption

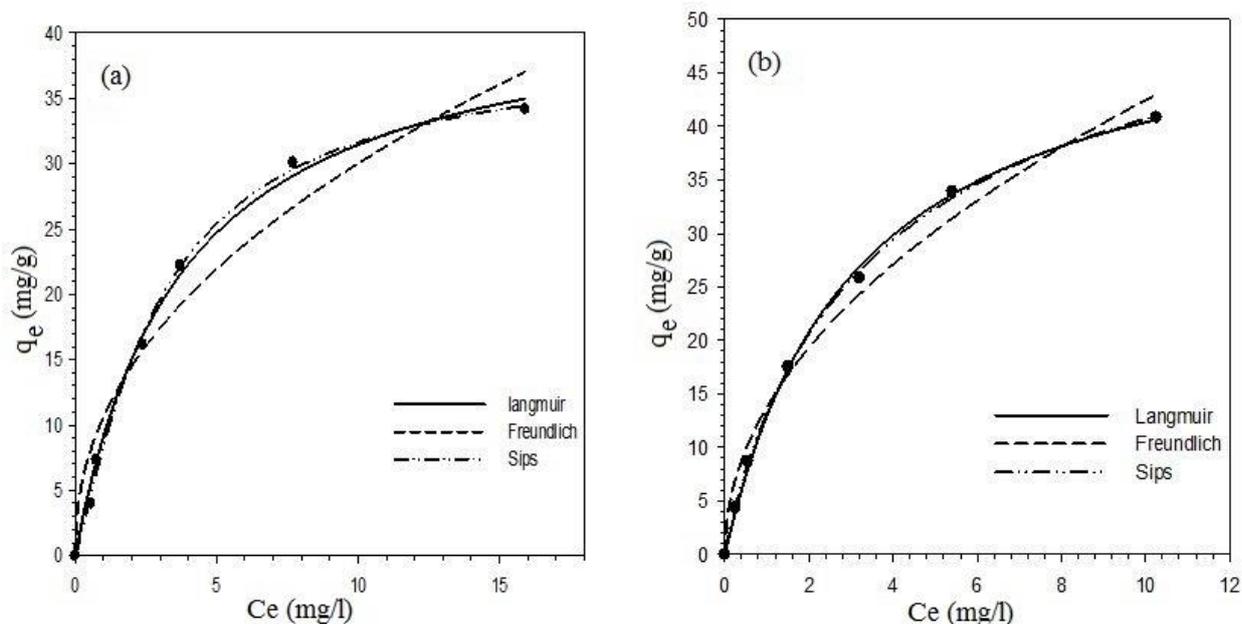


Figure 7. Fe (II) (a) and Cr (VI) (b) ions adsorption data and the fitted curves by Langmuir, Freundlich and Sips isotherms on the walnut shell activated carbon at 303 K.

Table 3

Equilibrium isotherm parameters for the removal of Fe (II) and Cr (VI) at T=303 K.

Isotherm models	Parameters	Fe (II)	Cr (VI)
Langmuir	K_L (L/mg)	0.267	0.3241
	q_{max} (mg/g)	43.22	52.87
	R_L	0.190	0.2311
	R^2	0.9953	0.9986
Freundlich	K_F (mg/g(L/mg ^{1/n}))	10.603	13.78
	N	2.21	2.04
	R^2	0.952	0.9837
Langmuir-Freundlich	K_{LF} (L/mg)	0.335	0.2576
	q_{max} (mg/g)	39.16	58.07
	B	1.1903	0.9011
	R^2	0.9978	0.9991

Table 4

Summary of Fe (II) and Cr (VI) ion adsorption on different adsorbents.

Metal ion	Adsorbent	Activator	Maximum C ₀ of metal (mg/l)	q _{max} (mg/g)	Temperature (K)	pH	Ref.
Cr (VI)	Walnut shell (Juglans regia)	Citric acid	52	30.992	293	2	[24]
	Rice husk	KOH-NaOH	39.51	34.7-32	293	5	[26]
	Palm kernel shell (Carbon nanotubes)	HNO ₃	0.5	8.25	-	4	[41]
	Sugarcane bagasse(raw)	-	500	5.75	298	2	[7]
	<i>Terminalia Arjunnuts</i>	ZnCl ₂	30	28.43	298	1	[11]
	Coconut shell charcoal	KOH	25	10.88	298	4	[16]
	Peanut shell	KOH	100	14.31	313	2	[19]
	Walnut shell	ZnCl ₂	100	43.12	313	2	This study
	Pomegranate peel (raw)	-	100	18.52	302	6	[27]
	Chitosan	-	50	28.7	293	4	[36]
Fe(II)	lignite	-	130	46.46	313	3.5	[6]
	Woodchips (pine and spruce)	ZnCl ₂	125	21	293	4	[4]
	Coir fiber waste	H ₂ O ₂	73.5	7.49	298	4.75	[42]
	Wooden charcoal (raw)	-	10	1.03	298	-	[43]
	Walnut shell	ZnCl ₂	100	39.25	313	4.5	This study

3-3-2. Binary adsorption

The results obtained from the absorption experiments for a binary system consisting of an equivalent concentration of Fe (II) and Cr (VI) have been shown in Fig. 8. As it is

observed from the figure, the absorption capacity of Fe (II) and Cr (VI) ions in single solution is greater from binary solution. That is because the adsorbent can provide a limited number of binding sites on its

surface, some of which are expected to be saturated by the competing ions, especially at high concentration. In comparison, the amount of Cr (VI) adsorption lies above the Fe (II) adsorption level over the entire range of composition. This can be contributed to the smaller radius of Cr (VI) in hydrated state and also its higher electronegativity [44]. However, in binary adsorption, according to ion exchange mechanism

between metals and active sites, the adsorbent can remove metals selectively. As seen from Fig. 8, the absorption capacity of iron ions is greater from chromium ion in binary solution. This might be due to stronger chemical interaction such as complexation between the adsorbent surface and Fe (II) through formation of iron chelates [45] which surpassed the Cr (VI) adsorption.

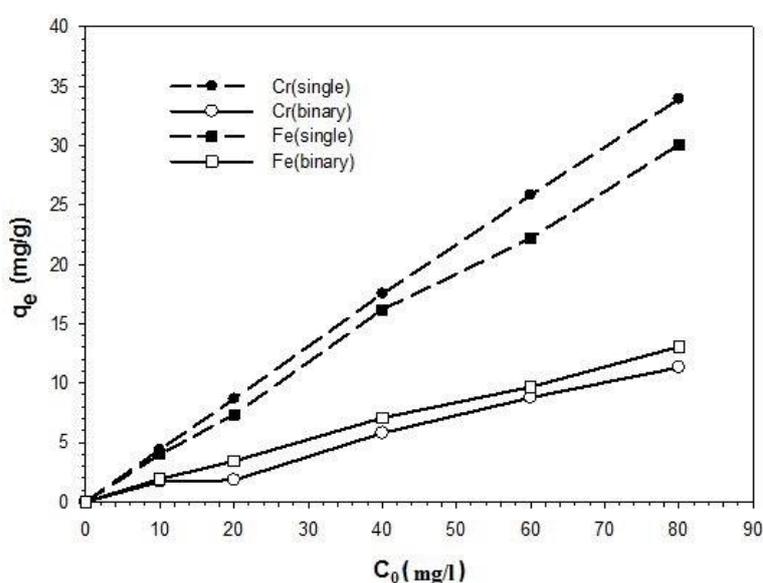


Figure 8. Fe (II) and Cr (VI) ions adsorption data in the single and the binary solution on the activated carbon.

To describe adsorption mechanism in a binary system, the data of metal ions adsorption onto the synthesized AC were fitted with extended Langmuir isotherm [46] according to equation (6):

$$q_{e,i} = \frac{q_{\max,i} K_{EL,i} C_{e,i}}{1 + \sum_{j=1}^n K_{EL,j} C_{e,j}} \quad (6)$$

The model parameters are different from those of single adsorption parameters. A multi-objective optimization (MO) process was used to determine the optimal model

parameters through the highest compliance with the experimental data. MO leads to a set of best solutions, which is named Pareto front and neither point at this curve is better than the other. Evolutionary algorithms (EAs) such as non-dominated sorting genetic algorithm (NSGA-II), which was presented by Deb *et al.* [47], as a technique of MO is an effective way to achieve a satisfactory convergence in curve fitting problems. In this study, two objective functions have been defined as mean square errors which are as follows:

$$f_1 = \frac{1}{n} \sum_{i=1}^n (q_{Fe,approximation} - q_{Fe,experimental})^2 \quad (7)$$

$$f_2 = \frac{1}{n} \sum_{i=1}^n (q_{Cr,approximation} - q_{Cr,experimental})^2 \quad (8)$$

Where f_1 and f_2 are the first and second objective function for Fe (II) and Cr (VI) ions adsorption respectively and n is number of data. An optimization problem was defined so that both objective functions are simultaneously minimized as much as possible. The isotherm constants were obtained by non-dominated sorting genetic algorithm and using binary

adsorption data. Nonlinear fit of experimental binary adsorption data at 303 K with extended Langmuir model are shown in Fig. 9, and Fig. 10 demonstrates the Pareto optimal front including a set of best solution. Among all the options, the solution that has the largest correlation coefficient was chosen and the isotherm constants were listed in Table 5. In the table, R-square has been calculated according to all of data and also based on the isotherm parameters, the cost of objective functions was estimated 0.76 and 0.72, respectively.

Table 5

The extended Langmuir isotherm constants for binary adsorption of Fe (II) and Cr (VI).

Parameters				R-square
q_{m1}	q_{m2}	$K_{EL,1}$	$K_{EL,2}$	
69.9798	66.7264	0.0047	0.0043	0.991

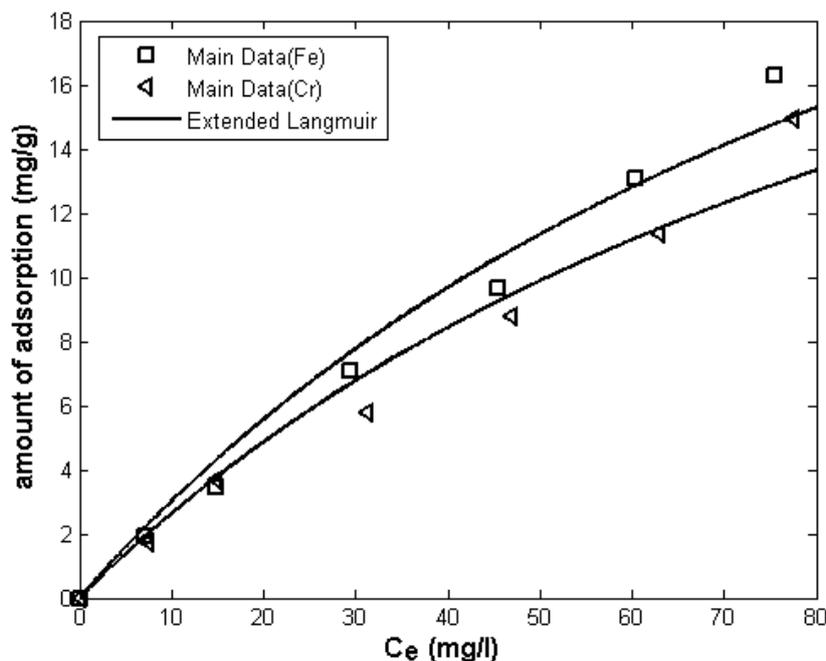


Figure 9. Experimental metal ions adsorption data in the binary mixture and the fitted curves by extended Langmuir isotherm on the activated carbon at 303 K.

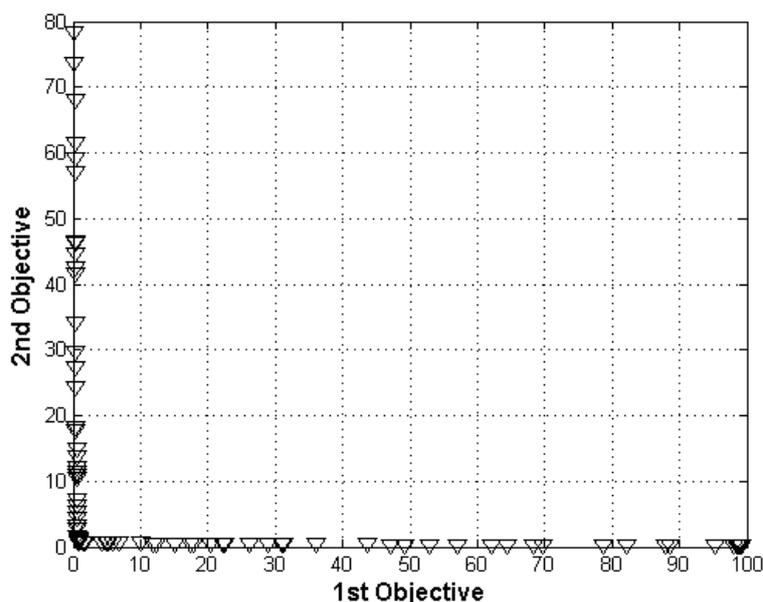


Figure 10. Pareto optimal front as a set of the best solution for binary adsorption curve fitting.

3-4. Adsorption kinetics

The study of adsorption kinetics describes the solute uptake rate which in turn controls the residence time of solute at the solid–solution interface [48]. Besides, it gives some information on how fast the adsorption of solute onto the adsorbent surface takes place. In the present work, in order to evaluate the adsorption kinetics of iron and chromium onto the synthesized adsorbent, experimental kinetic data were fitted to various kinetic models at 303 K.

In pseudo-first-order model, it is assumed that a weak physical interaction, which is created from weak collision between the adsorbed metal ions and the adsorbent surface, controls the adsorption process. The pseudo-first-order kinetic model can be presented by the equation (9):

$$q_t = q_e(1 - e^{-K_1 t}) \quad (9)$$

Where q_t and q_e (mg/g) denote the amounts of metal ions adsorbed after t minutes and at equilibrium state, respectively and K_1 (1/min) is the pseudo first order rate constant.

Many systems of adsorption follow the pseudo second order equation. The model is based on the assumption that absorption occurs due to chemical reaction between adsorbed ions and the adsorbent surfaces through covalence forces [48]. The model is given as follows:

$$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \quad (10)$$

Where K_2 (g/mg.min) is the rate constant of pseudo-second order equation.

In this study, we have also used pseudo-n-th-order model expressed by the equation (11) in which the order of adsorption reaction was considered as an adjustable parameter [49]:

$$q_t = q_e - [(q_e)^{1-n} + (n-1)K_n t]^{\frac{1}{1-n}} \quad (11)$$

The parameters n , K_n and q_e are three model parameters which were estimated by fitting kinetic data using a genetic algorithm code. The task was carried out as a minimization problem by definition of an objective function according to equation (12):

$$Error = \frac{1}{N} \sum_{i=1}^N (q_{\text{model}}(T, P) - q_{\text{exp}}(T, P))^2 \quad (12)$$

With the value obtained for the n parameter, 1.69 and 1.61 for Cr (II) and Fe (II), respectively, the pseudo- n -th-order kinetics model could accurately describe adsorption kinetics. The experimental kinetic data along with the predicted values by different kinetic models for the adsorption of Fe (II) and Cr (VI) ions onto the walnut shell-based AC have been represented in Fig. 11. Table 6 demonstrates the models parameters and calculated models correlation coefficients. It is clear from the table that the pseudo-second-order and the pseudo- n -th-order kinetic model have a higher correlation coefficient (R^2) than the other model for Fe (II) and Cr (VI) ions adsorption.

Reaction type kinetic models such as pseudo-first order and pseudo second order models cannot determine the diffusion mechanism. The intra-particle diffusion as

a mechanistic model was used to give some information about diffusion mechanism using the adsorption kinetics data. The model is expressed as follows [30]:

$$q_t = k_{id} t^{0.5} + c \quad (13)$$

In equation (13), k_{id} ($\text{mg.g.min}^{0.5}$) is the intra-particle diffusion rate constant.

Plot of q_t against $t^{0.5}$ gives the diffusion model rate constant. Existence of a multiline in this plot indicates that the adsorption process is controlled by several mechanisms. The plot has been shown in Fig. 12, appearing in the form of linearity, indicating a three-steps diffusion mechanism.

The first step, which has a steeper slope, is named the external surface adsorption or momentary adsorption step (Line not shown clearly in Fig. 12). The gradual absorption occurs in the second step when the rate of adsorption is controlled by intra-particle diffusion phenomenon. Finally, in the third step intra-particle diffusion is reduced due to the very low adsorption rate [50].

According to obtained results using intra-particle diffusion model in Table 6, correlation coefficients and rate constants calculated for the second stage are larger than the third stage due to quick uptake at the beginning of the adsorption process. Diffusion into the pores and surface of the adsorbent controls the rate of adsorption because of the very slow transfer rates.

Synthesis of a high characteristics activated carbon from walnut shell for the removal of Cr (VI) and Fe (II) from aqueous solution: single and binary solutes adsorption

Table 6

The kinetic models constants for Fe (II) and Cr (VI) ion adsorption on the activated carbon at T=303 K ($C_0=40$ ppm).

Kinetic Model	Parameters	Fe (II)	Cr (VI)
Pseudo first order	q_e (mg/g)	15.16	16.22
	K_1 (1/min)	0.076	0.132
	R^2	0.963	0.978
Pseudo second order	q_e (mg/g)	16.46	16.56
	K_2	0.007	0.017
	R^2	0.994	0.992
Pseudo n-th order	q_e (mg/g)	15.9	16.5
	K_n	0.016	0.044
	N	1.69	1.61
	R^2	0.999	0.998
Intra-particle-diffusion	$k_{id,1}$	0.9	0.16
	R_1^2	0.99	1
	$k_{id,2}$	0.38	0.23
	R_2^2	0.835	0.94
	q_{exp} (mg/g)	16.18	17.517

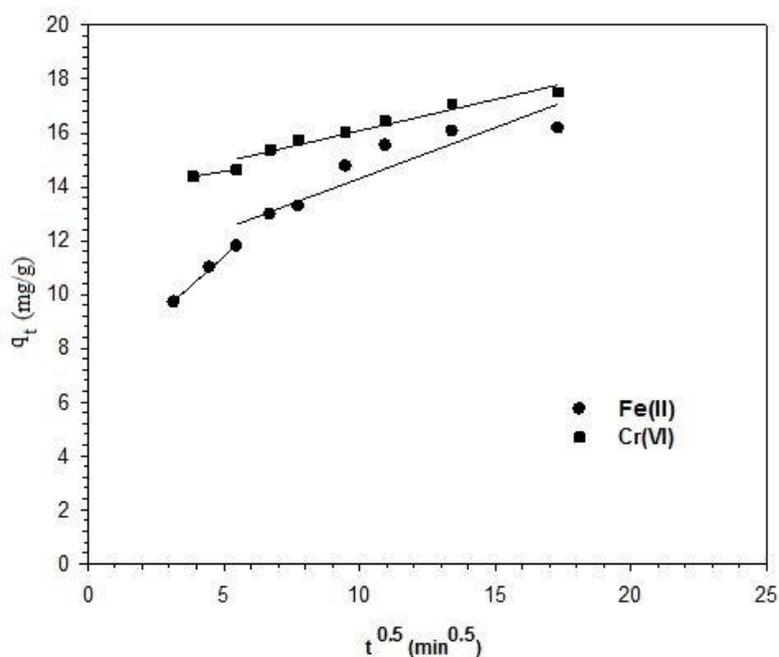


Figure 11. Kinetic data of Fe (II) and Cr (VI) ions adsorption on the walnut shell activated carbon and the fitted curves with Intra-particle diffusion model at T=303 K ($C_0=40$ ppm).

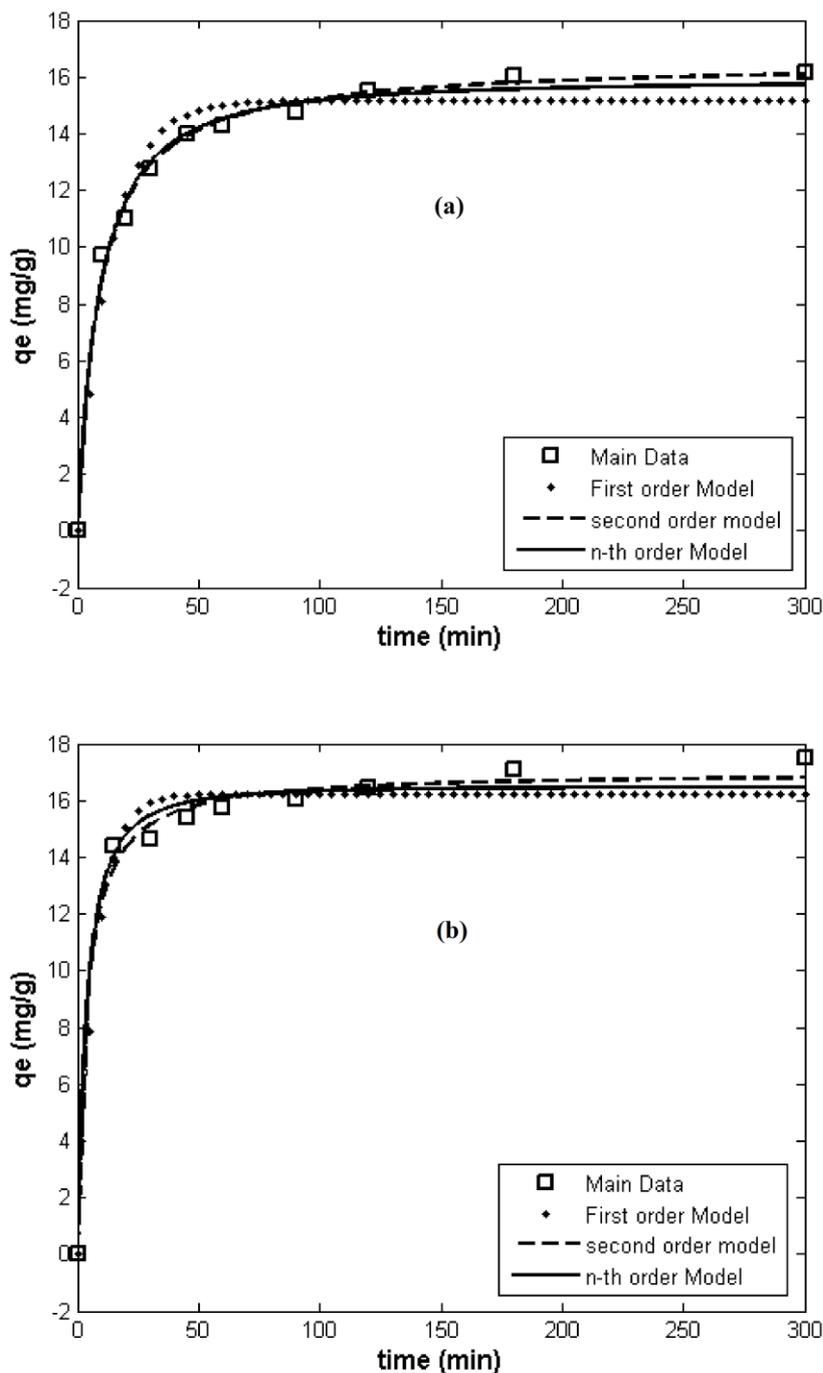


Figure 12. Kinetic data of Fe (II) (a) and Cr (VI) (b) ions adsorption on the walnut shell activated carbon and the fitted curves with pseudo n -th order, pseudo first and pseudo order kinetic model at 303 K ($C_0 = 40$ ppm).

3-5. Adsorption thermodynamics

The thermodynamic study of the adsorption process provides a valuable perspective about the thermal nature of the adsorption process. The measurement of thermodynamic

parameters such as Gibbs free energy (ΔG°), change in enthalpy (ΔH°), and change in entropy (ΔS°) is a vital section in the adsorption studies. ΔG° is calculated using the following equation (14):

$$\Delta G^0 = -RT \ln(K_{eq}) \quad (14)$$

where R (8.314 J.(mol K)⁻¹) is the universal gas constant, T (K) is the absolute temperature, and K_{eq} is thermodynamic equilibrium coefficient and can be calculated from the following equation (15) [51]:

$$K_{eq} = \frac{mq_e}{VC_e} \quad (15)$$

where q_e (mg/g) and C_e (mg/l) indicate concentration of metals adsorbed on the AC at equilibrium and metal equilibrium concentration in the aqueous phase. Also, ΔH⁰ (Kj/mol), the change in enthalpy and ΔS⁰ (J/mol.K), the change in entropy are represented as follows:

$$\ln(K_{eq}) = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (16)$$

The plot of ln (K_{eq}) versus 1/T was found to be linear and ΔH⁰ and ΔS⁰ values were

calculated from the intercept and slope of the plot by linear regression method, respectively. Thermodynamic parameters obtained from equation (16) are tabulated in Table 7 for metal ions of Fe (II) and Cr (VI) at the concentration of 10 mg/L. According to the obtained parameters, the negative value of ΔG⁰ confirms the possibility of the process and spontaneous nature of the adsorption process. It may be deduced from the positive values of ΔH⁰ that the sorption process is endothermic which had already been found by increasing adsorption capacity with rising the temperature. In addition, since the ΔH values for both adsorbates are above 80 kJ.mol⁻¹, chemical adsorption is the dominant mechanism [52] The positive value of ΔS⁰ is indicative of increased randomness at the solid-solution interface during the adsorption [53,54].

Table 7

Thermodynamic parameters for adsorption of Fe (II) and Cr (VI) ions on the walnut shell activated carbon.

Metal ion	T (K)	K _{eq}	-ΔG ⁰ (kJ/mol)	ΔS ⁰ J/(mol. K)	ΔH ⁰ (kJ/mol)
Fe (II)	293	8.496	5.212	34.05	134.68
	303	17.24	7.172		
	313	20.64	7.878		
Cr(VI)	293	15.66	6.700	70.266	262.58
	303	39.00	9.230		
	313	99.00	11.960		

4. Conclusions

The results of this study indicated that the AC prepared from walnut shells as an abundant solid waste by chemical activation demonstrate the well-developed porosity and high BET surface area (1223.44 m²/g). The characteristics of the synthesized walnut shell-based AC as well as their

capacities for adsorption of Cr (VI) and Fe (II) from aqueous phase were investigated. The percentage removal was found to depend on the time, temperature, pH and initial concentration of adsorbate. Maximum removal for Fe (II) and Cr (VI) was 96.2% and 99% at optimum pH of 4.5 and 2, respectively. It was also revealed that as the

temperature rose, the adsorption capacity for both heavy metals increased which confirms that the adsorption processes were endothermic. The adsorption kinetics and equilibria were described well by pseudo-nth-order and Langmuir-Freundlich isotherm models, respectively. The binary solutes adsorption was carried out to identify the preferential adsorption of a solute in the presence of other solute. Binary adsorption was described in terms of extended Langmuir models and the model parameters were found following an optimization procedure by genetic algorithm. The positive thermodynamic parameters, namely ΔG , ΔH , and ΔS showed that adsorption of Cr (VI) and Fe (II) on prepared activated carbons was spontaneous and endothermic under tested conditions. The capacity of the synthesized AC for adsorption of both metallic ions was remarkable compared to the other adsorbents reported in the literature. Thus the use of the low-cost adsorbent developed in the present study may contribute to the adsorption technology and economy for the removal of heavy metals from wastewater. The low-cost AC developed in the present study offers a promising adsorbent for commercial purposes in the future.

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