



Evaluation of adsorption efficiency of activated carbon/chitosan composite for removal of Cr (VI) and Cd (II) from single and bi-solute dilute solution

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ABSTRACT

The aim of this study was to evaluate the adsorption capacity of a novel activated carbon coated with chitosan for the removal of Cr (VI) and Cd (II) ions from single and bi-solute dilute aqueous solutions. In addition, the adsorption abilities of activated carbon (AC), chitosan (CH) and chitosan / activated carbon composite (CHAC) were compared. The adsorption studies were performed in a batch system, and the effects of various operating parameters such as solution pH, particle size and the dose of adsorbent were considered for the removal of Cr (VI) and Cd (II) via the Taguchi method. The equilibrium experimental data were well fitted to the Langmuir isotherm for single and bi-solute solutions. The adsorption capacities of the AC and CH adsorbents were improved by means of the synthesized CHAC composite. As expected, the competitive adsorption of metal ions on the CHAC surface led to a reduction in the adsorption capacity from 90.9 mg/g to 41.94 mg/g for Cr (VI) ions and 52.63 mg/g to 30.21 mg/g for Cd (II) ions, respectively. The adsorption potential of CHAC for Cr (VI) was greater than Cd (II) for the different metal solution-adsorbent systems. The kinetic studies indicated that the adsorption process was best described by pseudo-second-order kinetics for single and bi-solute solutions.

1. Introduction

Today, water contamination with different pollutants is a major environmental problem. Heavy metals and dyes are major water pollutants [1-12]. Heavy metals are widely distributed in the environment and are harmful due to their toxicity. They are non-biodegradable and their concentration is accentuated through bioaccumulation via the food chain in living organisms. Their accumulation causes different diseases and dysfunctions. Cadmium and chromium are toxic metals found in several industrial discharges and effluents. Cadmium is released into the environment through the combustion of fossil fuels, metal

production (zinc, iron and steel production), cement production, electroplating, and the manufacturing of batteries and pigments. The presence of cadmium (II) in water, even at very low concentrations, is extremely harmful to the aquatic environment; in humans, it causes muscular cramps, chronic pulmonary problems, renal degradation, proteinuria, skeletal deformity, and testicular atrophy [13]. The World Health Organization (WHO) guideline for Cd in drinking water is set at a maximum concentration of 0.003 mg/L [14]. Chromium found in the environment mainly exists in two oxidation states: Cr (III) and Cr (VI). Cr (VI) contamination is more concerning, as it is highly toxic, mutagenic and carcinogenic to living organisms; Cr (III) is generally less

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toxic and believed to be essential in glucose metabolism in mammals [15]. Chromium usually presents in the effluents of electroplating, tanning, mining, and fertilizer industries. The maximum chromium levels permitted in wastewater are 5 mg/L for Cr (III) and 0.05 mg/L for Cr (VI) [16]. Different technologies such as ion exchange, electrocoagulation process, and emulsion liquid membrane have been studied for heavy metal removal from industrial wastewaters [17-20]. Among these technologies, adsorption is more advantageous due to its high separation efficiency, low cost, and easy operation. Recently, the use of natural materials as the adsorbent for heavy metals removal from wastewater has gained considerable importance in the adsorption process [21-22]. Chitin, poly-N-acetylglucosamine, is a natural polymer found in several sources such as crustaceans and fungal cell walls. Chitosan, poly D-glucosamine, is the deacetylated form of chitin that has a large variety of applications in areas such as biochemistry, pharmacy, medicine, and agriculture as well as wastewater treatment [23]. The cationic character of chitosan is unique in that it is the only pseudo-natural cationic polymer. Chitosan has high nitrogen content in the form of amine groups. The amine and hydroxyl groups of chitosan have the capacity to absorb metals through several mechanisms including chemical interactions (such as chelation) and electrostatic interactions (for example, ion exchange or the formation of an ion pair). The kind of interaction depends on the metal type, its chemistry, and the solution pH [24]. In recent years, chitosan and its derivatives such as cross-linked chitosan, chitosan beads and composite chitosan have been studied as an adsorbent for the removal of dyes and heavy metal ions from aqueous solutions [24-30]. The main disadvantages of chitosan are related to its weak mechanical strength and its dissolution in acidic solution. To improve the performance of chitosan as an adsorbent, the modification of its physical and chemical properties is necessary. The immobilization of chitosan on common substances is a new method for its modification. If a proper and commercial material is used as a support for immobilizing the chitosan, its mechanical and chemical properties will be improved; also, much lower quantities of chitosan will be needed to build a new adsorbent. Recently, chitosan composites have been developed to adsorb heavy metals and dyes from wastewater. Different kinds of substances have been used to form a composite with chitosan such as sand, perlite, clay, and PVC beads [28-30]. Activated carbon adsorbents can adsorb many types of pollutants from industrial wastes because of their unique porous structure, high specific surface area, and high mechanical and chemical resistance, [31-

32]. Also, activated carbon can be used as a support for immobilizing the chitosan on its surface [33]. This research work analyzed the synergistic effects of chitosan and activated carbon on heavy metal removal from a multicomponent solution in the form of a chitosan/activated carbon composite. The adsorption ability of this new composite was investigated for Cr (VI) and Cd (II) removal from single and bi-solute solutions under different adsorption conditions. Also, the equilibrium and kinetics of the adsorption process were analyzed in order to understand the adsorption mechanism.

2. Material and methods

2.1. Materials

Chitosan flakes (CH) with a minimum of 80% degrees of deacetylation and a medium molecular weight of (750,000) were purchased from the Fluka Company. The $\text{Cd}(\text{NO}_3)_2$ and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ supplied by the Merck Company and the deionized water were used for the preparation of the metal solutions. The initial pH of the solution was adjusted with HCl and NaOH solutions (5 M) using a pH meter (Metrohm, 780). Commercially activated carbon pellets (AC), oxalic acid (0.2 M) and NaOH (0.7 M) were used for immobilizing the chitosan onto the activated carbon.

2.2. Synthesis of composite adsorbent

2.2.1. Stability of chitosan

Several researchers [28,34-35] have shown that chitosan is soluble in organic acids and to a certain extent, in mineral acids; however, its solubility depends on molecular weight and the degree of deacetylation of the chitosan. In our previous works, the stability of CH was investigated and the results showed that the applied CH was stable after 44 h of contact time in the acidic solution (pH = 1, 2) and remained in its original state as flakes. After this period of time, the CH began to gel and dissolve in the acidic media. Our previous results showed that the stability of CHAC in an acidic solution is 66 h [35-36].

2.2.2. Synthesis of chitosan/activated carbon composite (CHAC)

The chitosan/activated carbon composite (CHAC) was synthesized using a synthesis method described in our previous work [35-36]. Briefly, 20 g of AC was poured into 0.2 M of oxalic acid for 4 h. After washing with deionized water, filtration was done and the acid treated AC was dried in an oven. Then, ten grams of CH was added to 1 L of 0.2 M oxalic acid solution under continuous stirring at 40 °C to form a viscous gel. About 20 g of the acid treated AC was added slowly to the CH gel and stirred for 12 h at 40 °C. The CHAC composite

was prepared by the dropwise addition of the AC gel mixture into a 0.7 M NaOH precipitation bath. The beads were filtered and washed several times with deionized water to a neutral pH and dried in an air oven (50 °C).

2.3. Adsorbents Characterization

The adsorbents under study (CH, AC, and CHAC) were characterized with standard methods for different properties.

2.3.1. Bulk density and pH_{ZPC}

To measure bulk density, a 10 mL cylinder was filled to a specified volume with dried adsorbent. The cylinder was weighed. The bulk density was then calculated as follows [37]:

$$\text{Bulk density} = \frac{\text{weight of dry material (g)}}{\text{volume of packed dry material (cm}^3\text{)}} \quad (1)$$

In order to measure the pH_{ZPC} of the adsorbent, 50 mL of 0.1 mol/L NaCl solution was put into glass containers and the initial pH of these solutions was adjusted in the range of 1-12 using 0.1 mol/L HCl or NaOH solutions (Merck Co.). Then, 0.1 g of adsorbent was added to each container. The containers were agitated for 48 h at 25 °C. At the end of this time period, filtration was done and the final pH of the residual solutions was measured. The point in which the final pH equalled the initial pH of the NaCl solution was defined as pH_{ZPC} [35].

2.3.2. Specific surface area, surface chemistry, and morphology

The specific surface area (S_{BET}) and total pore volume of the adsorbents were determined from the adsorption-desorption isotherm of N_2 at 77 K. A Quantachrom NOVA 1000 surface area analyzer was applied to determine these parameters via the 3-point BET (Brunauer-Emmet-Teller) method. The surface chemistry of CH, AC, and CHAC were determined using Fourier transform infrared radiation (FTIR). The analysis was performed on PerkinElmer, Spectrum GX, under 4 cm^{-1} resolution, (sample/KBr = 1/100) within the range of a 400–4000 cm^{-1} wavenumber. The element analysis of CH and AC was determined by elemental analysis with a CHN analyzer (Perkin-Elmer 2400). The morphology of the CH, AC and CHAC composites were determined by direct measurement on the scanning electron micrographs (SEM, Vega II Tescan, MV2300).

2.4. Effect of removal parameters

In the removal experiments, CHAC was sieved and separated into three different particle sizes. All the dried samples of CH, AC, and CHAC were kept in a desiccator. The removal of Cd (II) from the single aqueous solution using CHAC was performed in our previous work [36]. In this study, the effects of three

operating parameters including solution pH, particle size, and dose of CHAC were investigated in three levels for the removal of Cr (VI) from the single solution. The Taguchi method was used for the experimental design. The degree of freedom related to the three sets of three-level adsorption parameters was six and in accordance with the Taguchi method; the standard orthogonal array L9, with three columns and nine rows, could be used for these experiments [38]. The experimental layout for these parameters using the L9 orthogonal array is listed in Table 1.

Table 1. Arrangement of parameters in L9 orthogonal array

Parameter s	pH	Adsorbent particle size	Adsorbent dose(g/L)
1	1	0.210	2
2	1	0.425	4
3	1	1.000	6
4	3	0.210	4
5	3	0.425	6
6	3	1.000	2
7	6	0.210	6
8	6	0.425	2
9	6	1.000	4

The removal experiments for Cr (VI) were conducted in a batch manner by mixing a measured weight of CHAC with a known particle size in 50 mL of metal solution (initial concentration 50 mg/L) with a known initial pH in 100 mL Erlenmeyer flasks. These flasks were shaken at 25 °C using an orbital shaker at 250 rpm for 2 h. After this time, the adsorbent was separated by means of Whatman filter paper (No. 42), and the final solution concentration was analyzed using an inductively coupled plasma (ICP) analyzer (Varian 735ES) in the aqueous phase. The removal percentage of Cr (VI) removed by CHAC was determined from the following equation:

$$\text{Removal percentage} = \frac{(C_0 - C_f)}{C_0} \times 100 \quad (2)$$

In this equation, C_0 and C_f are the initial and final metal ion concentration (mg/L), respectively. All the above-mentioned removal experiments were repeated two times, and the average values were reported.

2.5. Kinetic studies

Adsorption kinetic experiments for single and bi-solute solutions of Cr (VI) and Cd (II) ions were performed at a pH = 6.0, a temperature of 25 °C, an adsorbent dose of 2 g/L, and an agitating rate of 250 rpm. The operation conditions were selected based on our experimental works. The effect of the initial pH, adsorbent dose and adsorbent particle size was investigated for the removal of Cr (VI) and Cd (II) using AC and CH. The results indicated that the optimum operating conditions were an initial of pH=6, the particle size of the adsorbent =0.425 mm, and an adsorbent dose = 6

g/L for both metals removal. For the single solution, a certain dosage of AC, CH and CHAC was placed into the flasks containing 50 mL (50 mg/L) metal ion solution. For the bi-solute solution, a certain dosage of CHAC was placed in the flasks containing 50 mL metals solution (initial concentration of metals 50 mg/L: concentration ratio of Cr (VI) and Cd (II) was 1). The contents of the flasks were agitated on an orbital shaker for prescribed periods of time (5-150 min). After these time periods, the adsorbent was separated by Wattman filter paper and the solution concentration was analyzed using an inductively coupled plasma (ICP) analyzer. The metal uptake capacity, q , for each metal ion was calculated as:

$$q = \frac{V}{m}(C_o - C_t) \quad (3)$$

where q_t , C_t , V and m were the amount of solute adsorbed per unit weight of adsorbent (mg/g) at t (min), final metal ions concentration (mg/L), solution volume (L) and dry weight of adsorbent (g), respectively. The kinetics experiments were repeated two times and the average values were reported.

2.5.1. Kinetic models

In order to investigate the mechanism of adsorption, the kinetic models were exploited to test the experimental data. In this work, three general kinetic models including pseudo-first-order, pseudo-second-order and intra-particle diffusion (Waber–Morris model) were used to test kinetic data. These models are presented in Table 2.

Table 2. Kinetics models

Kinetic model	Equation
Pseudo-first-order ¹	$\log(q_e - q) = \log q_e - \frac{k_1 t}{2.303}$
Pseudo-second-order ²	$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$
Intra-particle diffusion ³	$q_t = k_{id} t^{0.5} + C$

¹ k_1 (min⁻¹) is pseudo-first-order rate constant, q and q_e are the amounts of solute adsorbed per unit weight of adsorbent (mg/g) at t (min) and equilibrium time, respectively.

² k_2 (g/mg min) is pseudo-second-order rate constant.

³ k_{id} (mg/g.min^{1/2}) is intraparticle diffusion rate constant

2.6. Equilibrium studies

For the assessment of adsorption equilibrium and to determine the adsorption capacity, the adsorption equilibrium for the single and bi-solute solution of Cr (VI) and Cd (II) ions were performed at a pH = 6.0, an adsorbent dose of 2 g/L, a temperature of 25°C, an agitating rate of 250 rpm and an equilibrium time of 24 h. The initial concentrations of Cr (VI) and Cd (II) for the single metal isotherm were 10–50 mg/L. For the bi-

solute system, one metal concentration was varied from 10 mg/L to 50 mg/L and the concentration of the other metal was kept constant (20 mg/L). After equilibrium time, the metal solution was filtered and the residual concentration of the metal ions was determined. The amount of Cr (VI) and Cd (II) adsorbed by adsorbents, q_e , was determined by Equation (3). These adsorption tests were repeated two times.

2.6.1. Adsorption isotherm

The three most widely used adsorption isotherms are the Langmuir, Freundlich and Dubinin–Radushkevich (D-R) isotherms as expressed in Table 3. In this study, the experimental data was analyzed in terms of these isotherms. The E (kJ/mol) parameter from the D-R isotherm gave information in regard to whether the adsorption mechanism was an ion-exchange or physical adsorption. If the magnitude of E was between 8 and 16 kJ/mol, the adsorption process was followed by an ion-exchange (chemical nature); if the values of $E < 8$ kJ/mol, the adsorption process had a physical nature [39].

Table 3. Isotherm models for equilibrium data

Isotherm	Model
Langmuir ¹	$\frac{1}{q_e} = \frac{1}{q_{max} \cdot K_L} \cdot \frac{1}{C_e} + \frac{1}{q_{max}}$
Freundlich ²	$\log q_e = \frac{1}{n} \log C_e + \log K_f$
Dubinin–Radushkevich ³	$\ln q_e = \ln q_m - \beta \varepsilon^2$ $\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right)$ $E = \frac{1}{(2\beta)^{1/2}}$

¹ q_{max} is maximum adsorption capacity of adsorbent (mg/g) and K_L is the Langmuir constant related to energy of adsorption (L/mg).

² K_f is the Freundlich constant related to adsorption capacity of adsorbent (mg^{1-(1/n)}L^{1/n}/g) and $1/n$ is the Freundlich–exponent related to adsorption intensity.

³ q_m is the theoretical saturation capacity (mol/g), β is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol²/J²), E is mean free energy (kJ/mol) of adsorption per molecule of the adsorbate.

3. Results and discussion

3.1. Adsorbents Characterization

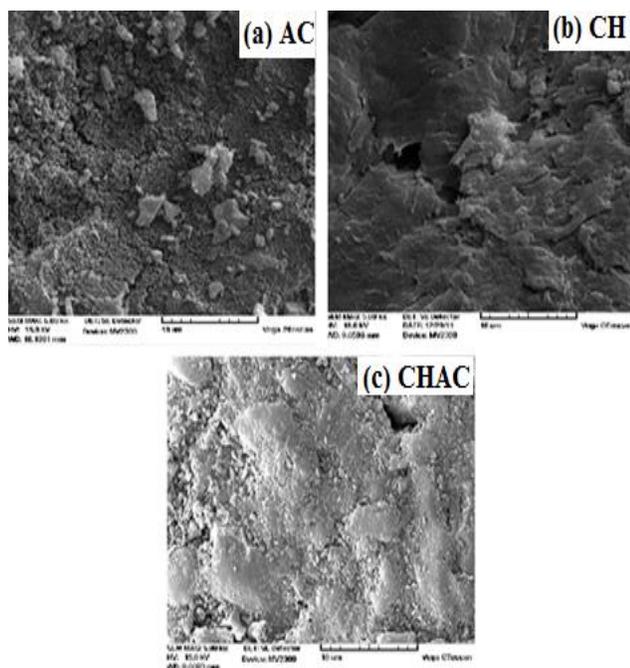
The physical and chemical properties of AC, CH, and CHAC are listed in Table 4. The surface area and total pore volume values were arranged in the following sequence: AC > CHAC > CH. The lower surface area and pore volume of CHAC was due to CH molecules blocking the pores of AC.

The improvement of the CH properties may occur because AC acts as a support for it.

Table 4. Characteristics of AC, CH and CHAC

Parameter	AC	CH	CHAC
Bulk density (g/cm ³)	0.60	0.21	0.27
BET surface area (m ² /g)	922.33	16.37	362.30
Total pore volume (cm ³ /g)	0.57	0.02	0.23
Average pore diameter (°A)	24.70	44.90	12.68
pH _{ZPC}	6.9	6.4	6.5
Element analysis of CH and AC		CH	AC
C		40.67%	87.29%
H		7.27%	0.62%
N		7.61%	0.35%

The result of the elemental analysis indicated that the nitrogen content of CH was about 8%, this parameter was related to the presence of amine groups in the CH structure [35]. The FTIR spectra of AC, CH, and CHAC were presented in Figure 1 of our previous work [36] and the description of these FTIR spectra was expressed in our work [36]. In brief, these spectra confirmed the presence of amine and amide groups in the chitosan structure. Also, the presence of carbonyl, lactonic and carboxyl, and carboxylic acid groups in the structure of the activated carbon has been determined. The peaks at 1548 cm⁻¹-1602 cm⁻¹ in the FTIR spectra of CHAC are the specific peaks for N–H scissoring from the amines and amides. These findings confirm that CH was successfully immobilized on AC [35-36]. Figure 1 shows the SEM microscopies of the AC, CH, and CHAC adsorbents. These images revealed that CH coated the surface of AC and reduced the pores of AC.

**Fig. 1.** SEM micrograph of: (a) AC, (b) CH, (c) CHAC

3.2. Effect of removal parameters

To analyse the results in the Taguchi method, the percentage of Cr (VI) and Cd (II) removal was selected as the performance characteristic of the process, and the optimum operating conditions were determined based on this parameter. The observed results for the effect of pH solution, adsorbent particle size and adsorbent dose on Cr (VI) and Cd (II) removal from a single component solution using CHAC are presented in Figure 2. The results indicated that the optimum operating conditions were a pH=6, the particle size of the adsorbent =0.425 mm, and the adsorbent dose = 6 g/L. Under these conditions, 100% of Cr (VI) and Cd (II) were removed from the dilute solution by CHAC after only 2 h. The results for cadmium removal were also presented in our previous article [36]. The pH-dependent metal removal can be mainly related to the functional groups of adsorbent and also to the metal chemistry. The pH_{ZPC} of CHAC was 6.5. At a pH < pH_{ZPC}, the surface charge of the adsorbent was net positive and could uptake anions by the electrostatic attraction mechanism; at a pH > pH_{ZPC}, the surface charge of the adsorbent was net negative [35]. In the acid media, HCrO₄⁻, Cr₂O₇²⁻ and H₂CrO₄ were the predominant species of chromium. In basic solutions, chromium exists in the form of CrO₄²⁻. If the pH ranged from 2 to 6, HCrO₄⁻ and Cr₂O₇²⁻ were predominant in equilibrium; but at a pH < 1, the main species was H₂CrO₄ [40]. Cadmium existed as a free Cd²⁺ species along the whole acid pH range. The metal complexes precipitated at a pH ≥ 7 and therefore, the separation may not be due to adsorption [41]. In an acidic pH (1-4), the surface charge of CHAC was positive and could attract chromium anions by electrostatic attraction. At a pH > 4, the surface of the adsorbent had a higher negative charge. But the maximum removal percent was achieved at a pH of 6. These results can be attributed to the complexation of Cr (VI) with the surface functional groups of CHAC. According to the experimental results, the strong pH-dependent adsorption indicated that the adsorption was dominated by the surface complexation model for chromium. For cadmium adsorption, in a low pH, the surface charge of CHAC was positive and could not attract Cd²⁺ cations; however, at high pH values, the surface of the adsorbent had a higher negative charge which resulted in a higher cadmium attraction. The obtained results showed that these three parameters affected the performance characteristic of the removal process, but the percentage contribution was different for each parameter. Therefore, the percentage contribution of these parameters should be evaluated. The ANOVA table (Analysis of variance) was used for this objective in the Taguchi method. In the ANOVA

table, the F- ratio could be used to determine which parameters had a significant effect on the performance characteristic. The calculated values of the F-ratio were compared with the F values predicted by the statistical F distribution (in Fischer tables) [42] at 95% confidence levels for CHAC. According to the rule, when the F

calculated in the ANOVA table was bigger than the standard F, the parameter was significantly influenced by the response variable at the respective confidence level. The results of the ANOVA are shown in Tables 5 and 6 for Cd (II) and Cr (VI) removal by CHAC, respectively [36].

Table 5. Results of ANOVA table for Cd (II) removal by CHAC [36]

Removal parameters	Sums of squares	Var (V)	F-ratio	Percent of contribution
pH	11119.36	5559.68	222.61	97.10
Adsorbent dose	108.96	54.48	2.18	0.51
Adsorbent particle size	121.44	60.72	2.43	0.62
Other/Error	49.94	24.97		1.75

Table 6. Results of ANOVA table for Cr (VI) removal by CHAC [36]

Removal parameters	Sums of squares	Var (V)	F-ratio	Percent of
pH	6324.89	3162.44	85.80	95.29
Adsorbent dose	80.24	40.12	1.08	0.09
Adsorbent particle size	80.90	40.45	1.09	0.10
Other/Error	73.71	36.85		4.49

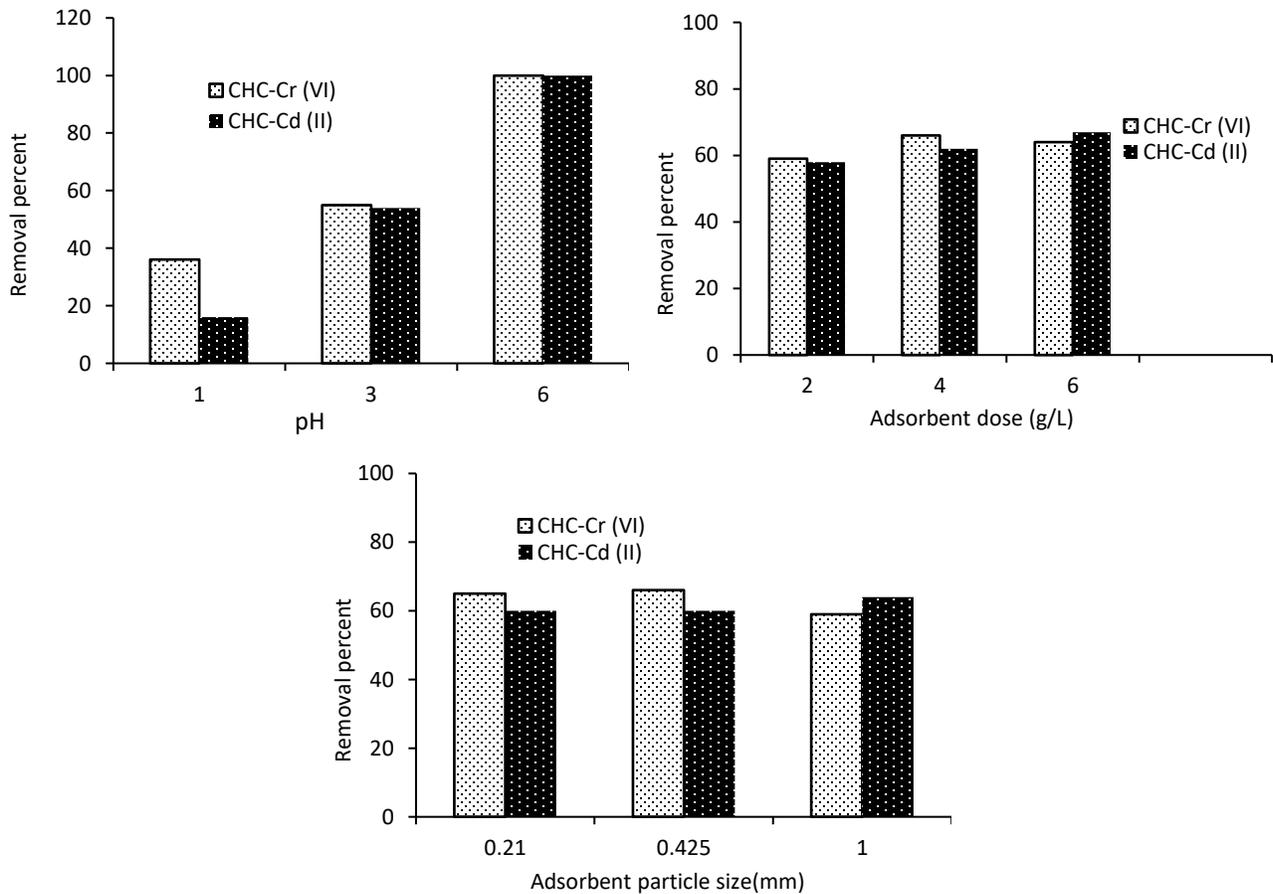


Fig. 2. Influence of (a) pH, (b) adsorbent particle size, (c) adsorbent dose on Cr (VI) and Cd (II) removal by CHAC

These tables indicate that the pH solution was the most significant removal parameter. According to these tables, the maximum percentages of error in these

results were 1.754 for Cd (II) and 4.497 for Cr (VI), which was not of significance. The Fisher tables indicated a 95% confidence for Cd (II) and Cr (VI) removal by CHAC,

$F_{0.05,2,2} = 19$. According to these values, the F calculated in the results in the ANOVA tables was bigger than the standard F for the pH solution. Therefore, this parameter had a significant effect on the performance characteristic for adsorption using CHAC. The F calculated in the ANOVA tables for the adsorbent particle size and the adsorbent dose were smaller than that of the standard F ; therefore, it can be concluded that these parameters did not have a main effect on the metals removal.

3.3. Comparison of adsorption performance of AC, CH and CHAC

3.3.1. Adsorption kinetics

Figure 3 shows the effect of contact time on the Cd (II) and Cr (VI) removal from a single component solution using AC, CH, and CHAC. The results demonstrated that the removal rate was faster for the first 5 min. As shown in this figure, the removal process reached equilibrium at 100 min for all adsorbents. The experimental data was tested in terms of pseudo-first-order, pseudo-second-order, and intra-particle diffusion kinetic models. The constants and regression coefficient (R^2) of these models are given in Table 7.

Table 7. Kinetic models parameters for single solute adsorption of Cd (II) and Cr (VI) by AC, CH and CHAC

	Pseudo-first-order				Pseudo-second-order			Intraparticle diffusion		
	$q_{e,exp}$ (mg/g)	k_1 (min ⁻¹)	q_e (mg/g)	R^2	k_2 (g/mg min)	q_e (mg/g)	R^2	k_{id} (mg/g min ^{1/2})	C	R^2
AC-Cd (II)	7.87	0.12	2.95	0.94	0.06	8.03	0.99	0.55	4.80	0.83
CH-Cd (II)	7.67	0.09	5.48	0.94	0.02	7.99	0.99	0.77	2.73	0.97
CHAC-Cd (II)	10.30	0.11	2.76	0.97	0.08	10.60	0.99	0.38	8.10	0.97
AC-Cr (VI)	12.30	0.04	1.35	0.98	0.09	12.50	0.99	0.13	11.1	0.98
CH-Cr (VI)	11.80	0.05	3.90	0.98	0.03	12.04	0.99	0.35	8.49	0.93
CHAC-Cr (VI)	12.50	0.68	0.26	0.96	0.48	12.63	1	0.03	12.2	0.93

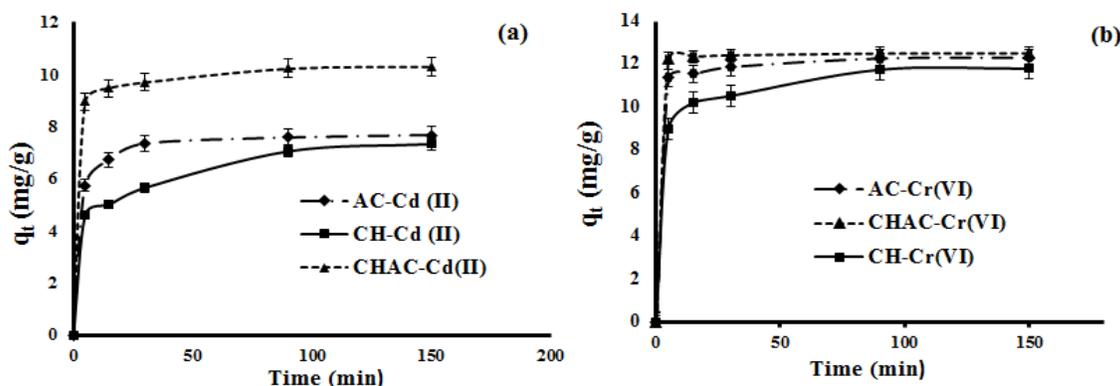


Fig. 3. Influence of contact time on removal efficiency from single solution using AC, CH and CHAN for (a): Cd (II), (b): Cr (VI)

For all adsorbent-metal systems, the pseudo-second order model had a high correlation coefficient ($R^2 \geq 0.99$). In addition, the calculated q_e from pseudo-second-order model was very similar to experimental q_e for Cd (II) and Cr (VI) adsorption by AC, CH, and CHAC. Therefore, the pseudo-second-order model was the best model to predict the kinetic behavior of Cd (II) and Cr (VI) adsorption. This suggested that the adsorption mechanism was a chemical adsorption for Cd (II) and Cr (VI) adsorption on the three adsorbents. The k_2 values for the adsorption by CHAC were higher than adsorption by AC and CH; this indicated that the metals adsorption by CHAC was faster. The overall reaction kinetics for the adsorption of Cd (II) and Cr (VI) was a pseudo-second-order process. However, this could not

be emphasized in regard to the rate-limiting step. It is always important to predict the rate-limiting step in an adsorption process to understand the mechanism of adsorption. Generally, the adsorption process involves three types of mechanisms:

- The liquid-film diffusion (external diffusion) involves the movement of adsorbate molecules from the bulk of the solution towards the external surface of the adsorbent.
- The adsorption of the adsorbate molecules on the surface of the porous adsorbent. This step is assumed to be very rapid and the binding process can be physical or chemical.

- In the intra-particle diffusion (internal diffusion), the adsorbate molecules move in the interior of the adsorbent particles.

The intra-particle diffusion model suggested by Weber and Morris was used for the probability of intra-particle and liquid-film diffusion mechanisms. The plot of q_t against $t^{0.5}$ can be employed to test the linearity of the experimental values. If the plot was linear and passed through the origin, the internal diffusion was the slowest (rate controlling) step in the adsorption process. But, if the plot was non-linear or linear but did not pass through the origin, it suggested that the adsorption process may be controlled by film diffusion and internal diffusion together. Based on these data, the intra particle diffusion model had high correlation coefficient values ($R^2 \geq 0.97$) for Cd (II) adsorption by CH and CHAC and Cr (VI) adsorption by AC. But the plots of q_t versus $t^{0.5}$ did not pass through the origin and have the intercept; therefore, the intra particle diffusion may

not be the rate controlling step. This indicated that the film/internal diffusion or/and chemical reaction controlled the adsorption rate of Cr (VI) and Cd (II) onto the AC, CH, CHAC surface.

3.3.2. Adsorption Equilibrium

The equilibrium results for Cd (II) and Cr (VI) adsorption from a single component solution (Fig. 4) by AC, CH and CHAC were fitted for the Langmuir, Freundlich and Dubinin-Raduskevich (D-R) isotherms. The values of the constants were calculated and are listed in Table 8. From the data presented in Table 8, it can be said that the Langmuir isotherm best fitted with the equilibrium data of Cd (II) and Cr (VI) adsorption on all adsorbents; this suggested that the present adsorption process was probably controlled by a monolayer adsorption process rather than multiple adsorption ones.

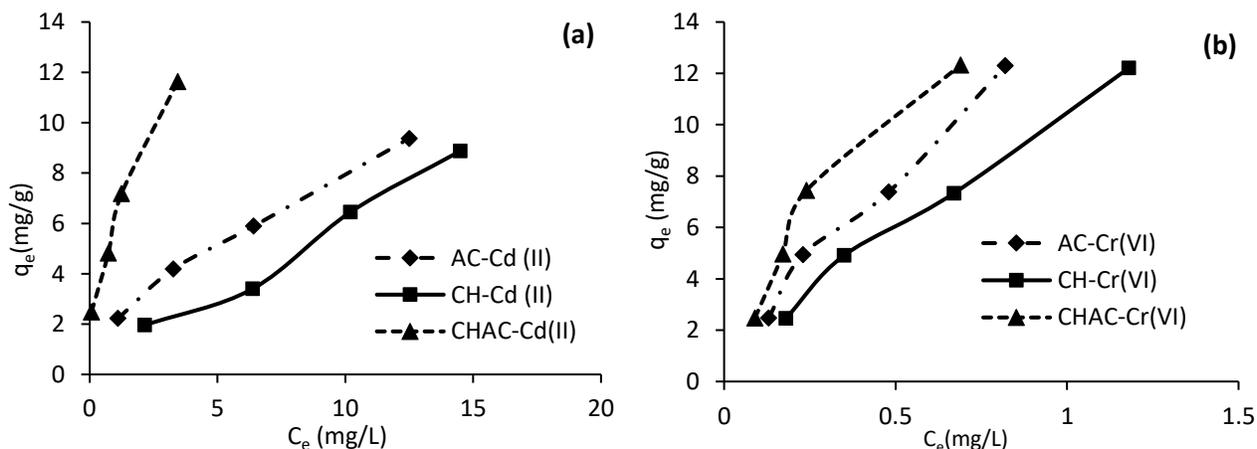


Fig. 4. Adsorption isotherms for (a): Cd (II) and (b): Cr (VI) adsorption from single solution by AC, CH and CHAC

According to the D-R isotherm parameters, the mean free energies E (kJ/mol) of adsorption per molecule of the adsorbate were 10.05 kJ/mol, 12.9 kJ/mol and 13.36 kJ/mol for Cd (II) adsorption and 13.1 kJ/mol, 9.41 kJ/mol and 12.5 kJ/mol for Cr (VI) adsorption using AC,

CH and CHAC, respectively; this corresponded to the ion-exchange process and electrostatic attraction (chemical nature). The maximum adsorption capacities of these adsorbents for Cd (II) and Cr (VI) are presented in Table 8.

Table 8. Equilibrium isotherms parameters for single solute adsorption of Cd (II) and Cr (VI) by AC, CH and CHAC

Adsorption system	Langmuir model				Freundlich model			D-R model		
	q_{max} (mg/g)	K_L (L/mg)	R^2	N	K_f ($mg^{1-(1/n)}L^{1/n}/g$)	R^2	β (mol^2/J^2)	q_m (mol/g)	R^2	E (kJ/mol)
AC-Cd (II)	10.30	0.24	0.98	1.70	2.07	0.94	4.5e-9	6.84	0.89	10.05
CH-Cd (II)	10	0.25	0.99	1.35	1.01	0.92	3e-9	5.19	0.88	12.90
CHAC-Cd (II)	50.50	0.11	0.98	1.34	4.93	0.95	2.6e-9	15.95	0.95	13.90
AC-Cr (VI)	52.63	0.39	0.99	1.21	14.40	0.97	2.9e-9	10.07	0.96	13.10
CH-Cr (VI)	41.60	0.35	0.99	1.11	10.60	0.97	5.7e-9	12.40	0.95	9.41
CHAC-Cr(VI)	90.90	0.43	0.98	1.56	17.80	0.90	3.2e-9	16.36	0.95	12.50

The maximum adsorption capacity of CHAC was higher than AC and CH for both metals adsorption and these

results indicated that by immobilizing CH on AC, the adsorption capacities of these adsorbents improved. In

addition, by employing this process, much lower quantities of AC and CH (they are expensive adsorbents) would be needed in the adsorption process which in turn changed the removal process into a cost-effective and environmentally friendly process. The maximum adsorption capacity of other adsorbents for Cd (II) and Cr (VI) are summarized in Table 9. As it can

be seen from Table 9, the maximum adsorption capacities of AC, CH and CHAC were higher than several other adsorbents. The comparison of q_{max} values indicated that these adsorbents exhibited reasonable capacities for Cd (II) and Cr (VI) adsorption from aqueous solutions.

Table 9. Adsorption capacity of different adsorbents for Cd (II) and Cr (VI) adsorption

Adsorbent	Liquid phase concentration (mg/L)	q_m (mg/g)		Ref.
		Cd (II)	Cr (VI)	
Orange peel-Fe ₂ O ₃	16	71.43	-	[8]
Chitosan	50-400	-	97.4	[26]
Urea-modified wheat straw	-	39	-	[41]
Olive stones	-	5.46	14.34	[43]
Turkish fly ash	0.2-6	0.29	-	[44]
Bentonite-iron oxide composite	10-700	63.29	-	[45]
Coffee grounds	10-700	15.65	-	[46]
Bamboo charcoal	20-100	12.08	-	[47]
PANI/CFs	1-56	-	18.1	[48]
Waste oil palm frond powder	-	-	90.09	[49]
Raw dolomite	5-50	-	10.1	[50]
Activated carbon prepared from peanut shell	10-100	-	16.26	[51]
Sweet potato peels	50-500	18	-	[52]
Fe ₃ O ₄ -SO ₃ H MNP	10-200	80.90	-	[53]
Bamboo charcoal grafted by Cu ²⁺ -N-aminopropylsilane complexes	2-12	-	17.93	[54]
Treated waste newspaper	5-70	-	59.88	[55]
Activated carbon prepared from longan seed	50-500	-	169	[56]
AC	10-50	10.3	51.6	This work
CH	10-50	10	41.6	This work
CHAC	10-50	52.63	90.9	This work

3.4. Adsorption of Cd (II) and Cr (VI) from bi-solute solutions

3.4.1. Adsorption kinetic

Figure 5 shows the kinetic adsorption profiles of Cd (II) and Cr (VI) on CHAC from bi-solute and single systems.

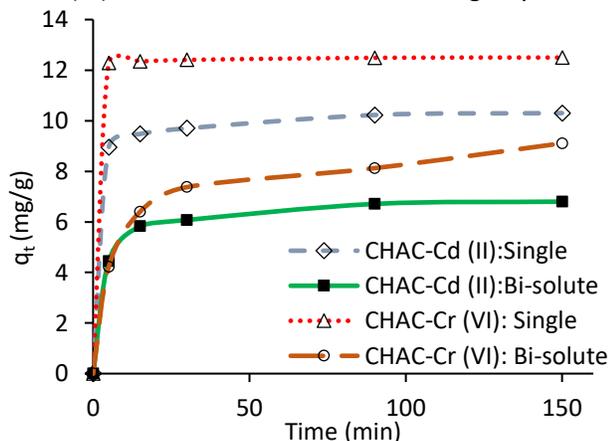


Fig. 5. Influence of contact time on Cd (II) and Cr (VI) removal from single and bi-solute solution by CHAC

The CHAC showed increasing Cd (II) and Cr (VI) adsorption with time, the same as that in the single systems. The results illustrated that in the binary system, the adsorption capacity of CHAC decreased 65% and 50% for Cr (VI) and Cd (II), respectively. This trend was a result of the competitive adsorption of Cd (II) and Cr (VI) ions. These results demonstrated that Cr (VI) was more sensitive to competitive adsorption than the Cd (II). These kinetic data were analyzed in terms of the pseudo-first-order, pseudo-second-order and intra-particle diffusion equations and the parameters of these equations are given in Table 10. Based on these results, the pseudo-second-order was the best model to predict the kinetic behavior of Cd (II) and Cr (VI) removal from bi-solute solutions with CHAC. In addition, the calculated q_e from the pseudo-second-order model was very similar to the experimental q_e for Cd (II) and Cr (VI) removal by CHAC. This suggested that the main adsorption mechanism was a chemical adsorption for these metals on CHAC. Also, the R^2 value of intra-particle model was low (0.8) for adsorption kinetics data of bi-solute systems. These results showed that the film diffusion was important for the adsorption of ions metals from bi-solute solution. The k_2 values for the adsorption

of two metals from single solutions were higher than that of the adsorption from bi-solute solutions; this indicated that the competitive adsorption led to a decrease in the adsorption rate.

3.4.2. Adsorption isotherms

The adsorption equilibrium isotherms obtained for Cd(II) and Cr(VI) ions by CHAC in the single and bi-solute system are shown in Figure 6. It was found that the adsorption of each metal decreased in the presence of another ion because of the competition of Cd (II) and Cr (VI) ions for adsorption on the active sites of the CHAC surface. These equilibrium data were analyzed with the Langmuir, Freundlich, and Dubinin–Radushkevich (D-R) isotherms; the constants of these models for bi-solute systems are summarized in Table 11. The results showed that the Langmuir isotherm best fitted with the equilibrium data of both metals adsorption on CHAC in the bi-solute system. The adsorption capacity of CHAC for Cr (VI) removal decreased from 90.9 mg/g in the single system to 41.94 mg/g in the bi-solute system; for Cd (II), it

decreased from 52.63 mg/g in the single system to 30.21 mg/g in the bi-solute system. In general, a mixture of different adsorbates may exhibit three possible types of behaviour: synergism (the effect of the mixture is greater than that of each of the individual adsorbates in the mixture); antagonism (the effect of the mixture is less than that of each of the individual adsorbates in the mixture); and non-interaction (the mixture has no effect on the adsorption of each of the adsorbates in the mixture). The $q_{\max,2}/q_{\max,1}$ ratios ($q_{\max,2}$ and $q_{\max,1}$ were the maximum adsorption capacity in the bi-solute and the single system from the Langmuir model, respectively) for the sorption of one metal in the presence of another metal were 0.46 for Cr (VI) and 0.57 for Cd (II) removal by CHAC, respectively. The ratios were all < 1, indicating that the adsorption of these metals was depressed by the presence of other metal ions in the bi-solute solution; hence, the effect of the mixtures seemed to be antagonistic. The $q_{\max,2}/q_{\max,1}$ for the Cr (VI) adsorption was smaller than the Cd (II) adsorption and this showed that Cr (VI) was very sensitive to the presence of Cd (II). It can be seen that the adsorption capacity followed the order as Cr (VI) > Cd (II) which was consistent with the order in single systems.

Table 10. Kinetic models parameters for bi-solute adsorption of Cd (II) and Cr (VI) by CHAC

Kinetic model	$q_{e,exp}$ (mg/g)	Pseudo-first-order			Pseudo-second-order			Intra-particle diffusion		
		k_1 (min ⁻¹)	q_e (mg/g)	R^2	k_2 (g/mg min)	q_e (mg/g)	R^2	k_{id} (mg/g min ^{1/2})	C	R^2
CHAC-Cd (II) Bi-solute	6.8	0.11	4.18	0.	0.05	6.89	0.99	0.64	3.38	0.85
CHAC-Cr (VI) Bi-	10.1	0.09	51.28	0.	0.02	9.9	0.99	1.14	2.31	0.85

Table 11. Equilibrium isotherms parameters for bi-solute adsorption of Cd (II) and Cr (VI) by CHAC

Adsorption system	Langmuir model			Freundlich model			D-R model			
	q_{\max} (mg/g)	K_L (L/mg)	R^2	n	K_f (mg ^{1-(1/n)} L ^{1/n} /g)	R^2	β (mol ² /J ²)	q_m (mol/g)	R^2	E (kJ/mol)
CHAC- Cd(II) Bi-solute	30.21	0.03	0.98	1.56	1.15	0.96	4.9e ⁻⁹	7.31	0.94	10.1
CHAC-Cr(VI) Bi-solute	41.94	0.05	0.98	1.41	2.87	0.9	5.1e ⁻⁹	9.94	0.95	9.9

4. Conclusions

In this paper, commercially activated carbon (AC), chitosan (CH) and chitosan/activated carbon composite (CHAC) were used as adsorbents for Cr (VI) and Cd (II) removal from single and bi-solute solutions. The Taguchi analysis of the experimental data showed that the solution pH had a significant effect on the removal process and the optimum operating conditions were as follows: pH = 6, particle size of the adsorbent = 0.425 mm and adsorbent dose = 6 g/L. Under optimum operation conditions, 100% of the Cr (VI) and Cd (II) were separated from the single-dilute solution with CHAC after 2 h. The Langmuir isotherm provided the best fit with the equilibrium data of Cr (VI) and Cd (II) removal on AC, CH in the single system and CHAC in the single and the bi-solute system. The CHAC had a higher adsorption capacity than that of AC and CH for Cr (VI) and Cd (II). The results showed that the adsorption capacity of CHAC for each metal decreased in the presence of another ion because of the competition of the Cr (VI) and Cd (II) ions; also, Cr (VI) was highly sensitive to this competitive effect. It was observed that the adsorption kinetics of Cr (VI) and Cd (II) on

AC, CH in single systems and CHAC in bi-solute systems could be suitably analyzed with the pseudo-second-order model. commercial spiral wound polyamide nanofilters was investigated for both synthetic and actual water specimens. The results are summarized as follows:

- 1- Both of the commercial polyamide spiral wound nanofilters can effectively remove Cr (VI) and nitrate from the contaminated water.
- 2- The interaction between the ions and charge of membranes influenced the pollutant removal efficiency. However, the NF-I showed a slightly better efficiency

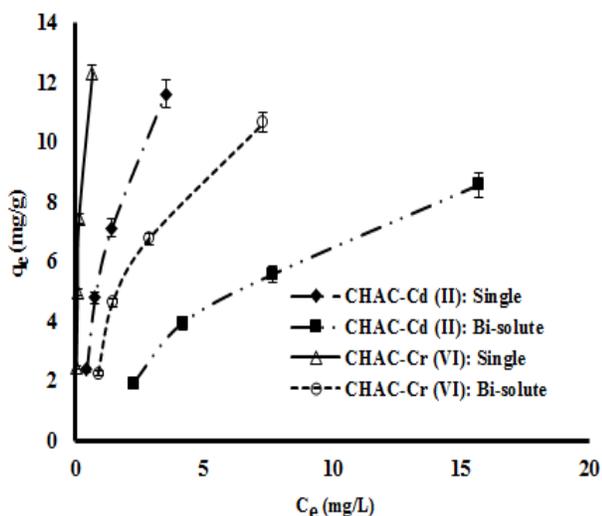


Fig. 6. Adsorption isotherms of Cd (II) and Cr (VI) adsorption from single and bi-solute solution by CHAC

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