

Comparison of Chitosan-Based Biocomposites for Remediation of Water with Cr(VI) Ions

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ABSTRACT: Chitosan/Fly Ash (CFA) and Chitosan/Activated Carbon (CAC) biocomposites were compared in terms of their performances for the removal of Cr(VI) ions from aqueous solutions. SEM and FT-IR images of both new synthesized adsorbents were also obtained. The removal of heavy metal, ion was carried out via batch adsorption process and the effects of parameters such as the amount of adsorbent (0.01-0.1 g), contact time (5-180 min), pH (1.0-5.0), and initial concentration (5-50 ppm) on adsorption were investigated. Both biocomposites had reached equilibrium in 30 minutes at a pH value of 3.0. The experimental data were evaluated in terms of isotherm models and it was indicated that Freundlich isotherm well fitted to the data. The maximum adsorption capacities of CFA and CAC were found as 23.6 and 24.4 mg/g, respectively. The adsorption process for Cr(VI) removal by CFA and CAC was also investigated in terms of kinetics models. It was found that both adsorbents were in accordance with the pseudo-second kinetics model and the related coefficients were calculated. It was determined that the biocomposites had higher efficiency for the removal process and when the performance of both biocomposites was compared, CFA, as a more natural residue-based sorbent, had a removal performance close to that of CAC.

KEYWORDS: Chitosan; Fly ash; Activated carbon; Cr(VI); Biocomposite.

INTRODUCTION

Heavy metal including water as a discharge of industrial processes causes serious problems regarding environment and human health. Among these heavy metals, chromium with its two oxidation states resulting in various industrial applications such as leather tanning, metal finishing, etc. is defined as a toxic pollutant. Especially Cr(VI) which is known as a carcinogen is more toxic than its trivalent state. Among many conventional methods, such as ion-exchange, membrane, coagulation-precipitation, etc., adsorption processes can offer significant advantages including availability,

profitability, ease of operation and efficiency. A variety of natural and synthetic materials have been used as Cr(VI) sorbents including nanoparticles [1,2], activated carbons [3,4,5], biological materials [6], zeolites [7], chitosan [4,8], and nanomaterials [9,10]. Unfortunately, these sorbents can also suffer from a number of disadvantages, including, high cost, low adsorption capacity and/or difficulties associated with separation and removal following treatment. The application of polymeric materials and natural residues having biodegradable and easy to handle structure for the adsorption process

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becomes attractive [11-15]. Therefore, using composite biosorbents as biocomposites takes considerable attention for the removal of heavy metals, dyes and other micropollutants in aqueous environment.

In our study, abundantly present natural fly ash and commercially available activated carbon were both modified with chitosan as biocomposites and their performances to remove Cr(VI) from aqueous solutions were compared by taking different parameters into consideration.

EXPERIMENTAL SECTION

Chemicals

Chitosan (deacetylated chitin, Poly(D-glucosamine) was purchased from Sigma Aldrich (USA) with 75-85 % deacetylation rate. Fly ash was obtained as a waste material from Izmir Aliaga Refinery plant in Turkey the content of which is given in Table 1. Moreover, activated carbon was also purchased from Merck (German). Cr(VI) solution was prepared from $K_2Cr_2O_7$ salt (Merck, German) and pH adjustments were done with HCl or NaOH purchased from Merck (German). All chemicals used for the experiments were of analytical grade.

Preparation of Chitosan based biocomposites

Chitosan powder was dissolved in acetic acid solution of 2wt% with a glass-rod. Fly ash was screened with a sieve of 100 mesh to get homogeneous particle size. Then, 20 g of fly ash were activated with 100 mL of 5 M H_2SO_4 at 30 °C for 12 h in a flask. The suspension was filtered off and then washed several times with double-distilled water [16,17] and dried in an oven at 60°C for 8 h prior to use. The activated fly ash was added to the chitosan solution to obtain composite with a ratio of 40 wt%. They were agitated for 45 min at room temperature and washed with distilled water until neutrality, got dried in 50 °C in an oven [18-20] and the final biocomposite was called chitosan coated fly ash as "CFA". The same procedure was applied for activated carbon and the final biocomposite was called chitosan coated activated carbon as "CAC".

Adsorption Studies

The removal of Cr(VI) ions from aqueous solutions was performed as batch experiments. After preparing the stock solution of Cr(VI) from the salt of $K_2Cr_2O_7$

in a concentration of 100 ppm, the other concentrations of Cr(VI) solutions were diluted from this stock solution. The batch experiments were carried out at 25 ± 1 °C in shaker at an average agitation speed of 200 rpm. 25 mL of Cr(VI) solutions were mixed with appropriate amount of CFA and CAC in erlenmeyer flasks. The supernatants were filtered through 0.45 μm Whatman filter papers and Cr(VI) concentrations were determined by using UV-visible spectrometer (Shimadzu UV-1700). The pH adjustments were carried out with 0.1 M HCl and 0.1M NaOH via Orion 900S2 model pH meter. The amounts of Cr(VI) ion sorbed at equilibrium by the both biocomposites were calculated using the formula:

$$q_e = (C_o - C) v / w \quad (1)$$

RESULTS AND DISCUSSION

Characterization of Biocomposite Adsorbents

The SEM images of raw materials and their biocomposites were taken. As modifying the fly ash and activated carbon by chitosan, rough surface of chitosan was changed by intercalation of fly ash particles which improved the structure by increasing the contact area of the biosorbent. The similar situation was observed for the CAC biosorbent and the adsorption capacities of both biocomposites were also improved when compared to their unmodified forms (Fig. 1).

The Brunauer–Emmett–Teller (BET) surface areas, pore volumes and sizes of samples were measured by standard multipoint techniques using Gemini VII 2390 V1.03 equipment (Micromeritics Instrument Corporation). The samples were exposed to a degassing process conducted at 423 K under vacuum for 2 h to attain a constant weight. The specific surface area, average pore diameter and total pore volume of activated fly ash were measured as 26.95 m^2/g , 6.203 nm and 0.00418 cm^3/g , respectively and those of active carbon were measured as 921 m^2/g , 0.5 nm and 0.00667 cm^3/g , respectively.

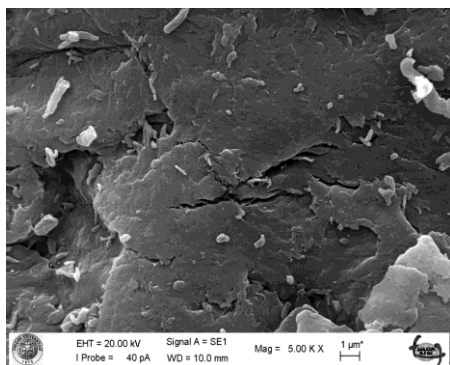
Effect of biocomposite amount

In order to determine the maximum possible Cr(VI) removal, it is necessary to find the optimum amount of the sorbent. In this regard, 25 mL of Cr(VI) solution with 40 ppm was mixed with varying amounts of composite adsorbents (0.01-0.1 g). The percentage of sorption increased with increasing amount of sorbent until

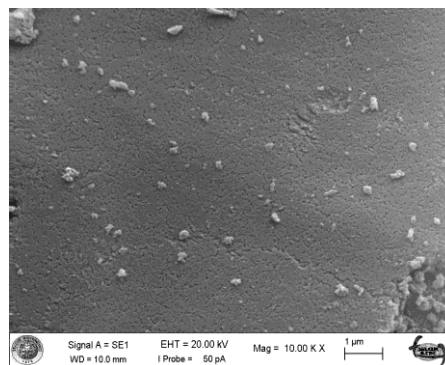
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Table 1: Chemical Content of Fly Ash.

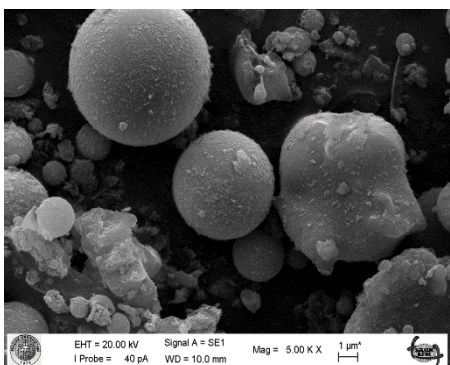
Elements	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Others
Content%	53.75	19.88	6.89	5.67	1.92	1.95	9.94



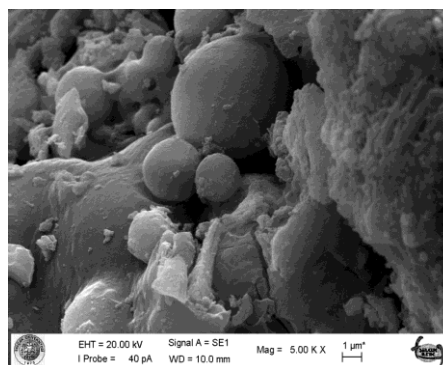
(a)



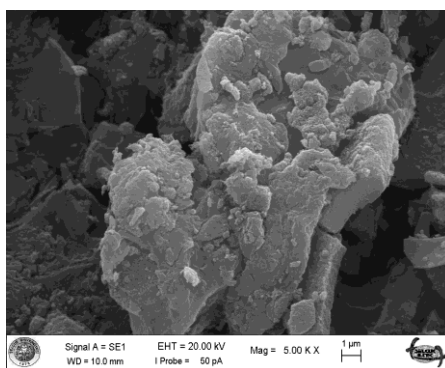
(b)



(c)



(d)



(e)

Fig. 1: SEM images of (a) chitosan, (b) activated carbon, (c) fly ash, (d) CAF and (e) CAC.

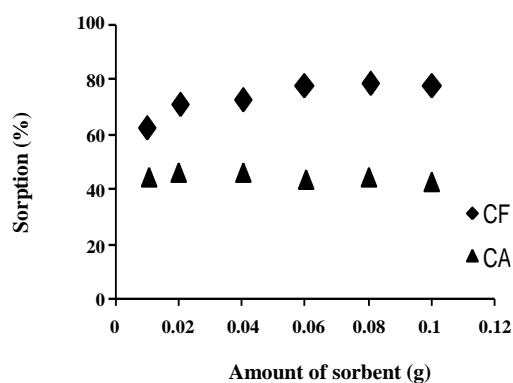


Fig. 2: Effect of amount of sorbent on the removal of Cr(VI).

it reached an equilibrium. Therefore, 0.04 g of composite adsorbent was selected as the optimum amount of sorbent as the plateau sorption percentage was obtained with this amount (Fig. 2) and using further amount of biocomposite does not alter the sorption percentage [21].

Effect of Contact time

The effects of contact time at room temperature on the sorption of Cr(VI) on all adsorbents are depicted in Fig. 3. The experiments were carried out by removal of 40 mg/L Cr(VI) in 25 ml of solution at pH 2.0, using 0.02 g/L of CFA and CAC. As can be seen increasing the contact time improved amount of adsorbed Cr(VI) metal ions significantly and reach equilibrium in 30 min for both adsorbents. In further contact time, there is no significant change in Cr(VI) adsorption percentage. Due to saturation of exterior surface, the Cr(VI) ions were exerted onto the pores of the biocomposite particles and were adsorbed by the interior surface of the particle. After these times, sorption rate becomes slow and leads to a smooth and continuous saturation curve [22].

Effect of pH

Since Cr(VI) occurs in nature in the forms of CrO_2^{-4} , $\text{Cr}_2\text{O}_2^{-7}$, HCrO_4^{-} and H_2CrO_4 . The effect of pH on the sorption of Cr(VI) ions onto the prepared chitosan biosorbents is depicted in Fig. 4. It can be resulted from the graph that which form of Cr(VI) was adsorbed with the biosorbents at which pH value of the solution. For CAC, high sorption percentages were observed in the acidic pH region (~ 1.0) whereas an inverse behaviour of lower adsorption rate at pH value of 1.0 was observed for CFA. However, the sorption rate also increases for CFA at around pH value of 3.0. It is considered that the form of

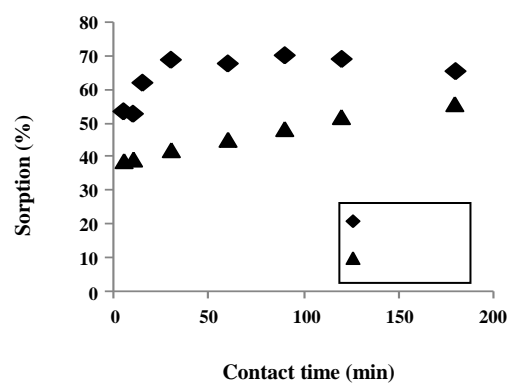


Fig. 3: Effect of contact time on the removal of Cr(VI).

Cr(VI) at this pH values was significantly $\text{Cr}_2\text{O}_2^{-7}$ form [18, 23-27].

Adsorption Isotherm Models

Experimental adsorption data were analyzed by two commonly known isotherm models such as Langmuir and Freundlich. Langmuir isotherm model is a model that best defines the situations where adsorption occurs on homogeneous surfaces and is described with the equation indicated in Table 2 where, C_e : is the concentration of Cr(VI) at equilibrium (mg/L), A_s : is the Langmuir adsorption capacity (mg/g), K_b defines Langmuir adsorption coefficient (L/mg) [13,15,18, 25-30].

Freundlich adsorption isotherm model, on the other hand, expresses adsorption phenomenon on heterogeneous surfaces the linearized equation of which is given in Table 2. Here, C_e : is the concentration of Cr(VI) at equilibrium (mg/L), K : is the Freundlich sorption capacity (mg/g) and n defines the isotherm coefficient [4-8, 25-30].

As shown in Table 2, adsorption isotherms modeling was in good agreement with the experimental data. The sorption of Cr(VI) by CFA and CAC can be said to be favorable with Freundlich isotherm model since the values of $1/n$ lying between 0 and 1. When the correlation coefficients (R^2) were taken into consideration, the Freundlich isotherm model results in higher R^2 indicating the best fit of Freundlich isotherm to the experimental data [26-30].

Adsorption Kinetics

The kinetics models are generally applied in order to predict the rate of adsorption process which can be useful for modeling of the removal system. Pseudo first-order and second-order kinetics are usually used to evaluate the experimental data [13].

Table 2: Linear Forms of Isotherm Models and Their Calculated Coefficients.

Isotherm Model	Linear Equation	Plot	Parameters		
			A_s	K_b	R^2
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K_b A_s} + \left(\frac{1}{A_s}\right) C_e$	(C_e/q_e) vs. C_e	A_s	K_b	R^2
CFA			0.454	314.1	0.834
CAC			0.469	308.6	0.951
Freundlich	$\log q_e = \log k + \frac{1}{n} \log C_e$	$\log q_e$ vs. $\log C_e$	K	n	R^2
CFA			1.087	3.352	0.995
CAC			4.54	2.524	0.987

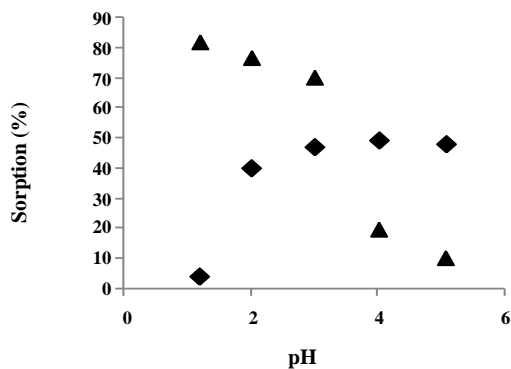


Fig. 4: Effect of pH on the removal of Cr(VI).

Pseudo first-order kinetics

The rate of adsorption process is dependent on the capacity of adsorbent if pseudo-first order kinetics is followed according to the Equation 2 which has a linearized form given in Equation 3:

$$\frac{dq_t}{dt} = k_{ad}(q_e - q_t) \tag{2}$$

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_{ad} t}{2.303}\right) \tag{3}$$

where q_e and q_t are the amounts of adsorbate adsorbed at equilibrium and at any time t , respectively (mg/g) and k_{ad} (L/min) is the pseudo first-order rate constant of adsorption process. Pseudo first-order kinetics model is just used to predict k_{ad} which is considered as mass transfer coefficient in design calculations [13, 24, 27].

Pseudo Second-Order kinetics

Since pseudo first-order kinetics model just gives k_{ad} and q_e cannot be predicted by this model, pseudo second-order kinetics model, as given in Equation (4) is tested to predict q_e :

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{4}$$

Where k_2 (g/mg.min) is the second-order rate constant. When this equation is integrated, Equation (5) is obtained with the limit conditions from $t = 0$ to t and from $q_t = 0$ to q_t :

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{5}$$

When a graph of t/q_t versus t is drawn, then a linear line is obtained and q_e as well as k_2 can be calculated.

For this adsorption process, the calculated data belonging to both kinetics models are given in Table 3. According to this data, especially taking R^2 values of the models into consideration, it can be resulted that pseudo second-order kinetics model explains the adsorption of Cr(VI) ions by CFA and CAC better than pseudo first-order model in accordance with the literature [13, 27, 30].

CONCLUSIONS

Adsorption equilibrium experiments were carried out as a function of contact time, amount of biocomposite, pH, and concentration. The adsorption capacity of Cr(VI) from aqueous solutions on CFA (23.6 mg/g) which was prepared from a waste material was approximately as high as that of CAC (24.4 mg/g) which is well known

Table 3: Calculated coefficients of kinetics models.

	Pseudo first-order kinetics model			Pseudo second-order kinetics model	
	$k_{ad} \cdot 10^2$	q_e	R^2	$k_2 \cdot 10^2$	R^2
CFA	2.14	11.365	0.954	0.44	0.998
CAC	2.03	26.533	0.834	0.13	0.992

commercial adsorbent at different initial Cr(VI) concentrations. The experimental data of these biocomposites were well defined with Freundlich isotherm model. The equilibrium time of Cr(VI) adsorption was found to be 30 min. Composite adsorbent had the highest adsorption efficiency when the ratio was 40 wt%. The maximum adsorption capacity of Cr(VI) took place at the initial pH 3.0. In terms of kinetics models, the adsorption data for this removal process were best explained with pseudo second-order kinetics model. Consequently, assessment of such a waste material as a biocomposite sorbent for the removal of Cr(VI) is valuable and can be further studied with other heavy metals.

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