Determination of Adsorption Characteristics of Orange Peel Activated with Potassium Carbonate for Chromium(III) Removal

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Abstract: In this study, Cr(III) removal from aqueous solutions was investigated by using the batch adsorption method. Orange peel activated with potassium carbonate (OPAPC) was used as the adsorbent because of the fact that adsorption capacity was higher when orange peel was activated with potassium carbonate, instead of both original orange peel and orange peel activated with phosphoric acid adsorbents. In order to determine optimum adsorption conditions, adsorbent concentration (2-15 g/L), pH (3-7), temperature (298-318 K), contact time (10-240 min) and initial concentration of Cr(III) (5-50 mg/L) were investigated for Cr(III) removal from aqueous solutions using OPAPC. The equilibrium data were evaluated using the Langmuir and Freundlich model equations and the kinetic data were evaluated with pseudo first and second order kinetic models. In addition, the adsorption thermodynamics of the proposed method in optimum conditions was investigated.

Keywords: Chromium, adsorption, orange peel, activation.

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INTRODUCTION

In general, heavy metals in the aqueous solutions and other samples produce a health risk for the environment and living organisms. Chromium (Cr) is an important pollutant especially for the environment. The metal coating, leather, wood protection, and textiles are the main uses of it. In principle, Cr is present in two different forms in nature such as Cr(III) and Cr(VI) (1). Cr(III) and Cr(VI) have different chemical, epidemiological, and toxicological properties. Cr(III) required for lipid and sugar metabolism is not necessary for plants, but it is necessary to a certain extent for human and animal health. However, more Cr uptake than required amount causes serious health problem in the living organisms (2, 3). For these reasons, determination of chromium amount and its removal from any matrix is an important task (4).

Among the methods used for treatment of wastewater, adsorption is preferred because of the ease of application and high removal efficiencies (5). However, in large-scale industrial applications, the cost of the process is as important as the cost of remediation. When evaluated in this context, interest in economic and environmental wastewater treatment methods based on adsorption is increasing with the use of economically unstable initiators in the preparation of adsorbents. Agro-agricultural by-products, which can be used as an alternative to active carbon these days, and materials obtained from wastes are paid attention because they are economical, they have efficiency in treatment and high metal adsorption capacity (6). The removal of wastes without harming the environment is also closely related to the economy as well as the environment and human health.

There are a number of works showing that natural and agricultural by products can be used effectively instead of biosorbents to remove the water toxic metals (7, 8). One of the most abundant wastes in food industry is the orange peel. In general, orange peel is used to remove the metal ions especially cadmium, lead, and copper from aqueous solutions (9-13). Studies in the literature have shown that physical and/or chemical activation improves the adsorbent properties of the orange peel such as porosity and surface area, and increases the number of available active sites. Furthermore, due to the soluble organic compounds consisted of the unmodified plant wastes; they can create high chemical oxygen demand (COD) and biochemical oxygen demand (BOD) in the aqueous solutions. The high level of these values can cause a reduction of oxygen in the aqueous solutions which can threaten the living in the aquatic environment (6, 14). In the last decades, K_2CO_3 has been widely used as a basic chemical activation element because of the fact that it is environment friendly and the bases such as KOH and NaOH are corrosive and toxic (15).

In this work, Cr(III) removal from synthetically prepared aqueous solutions using an adsorbent of orange peel activated with potassium carbonate (OPAPC) was performed in batch adsorption method. In principle, adsorption studies were conducted with original orange peel, orange peel activated with phosphoric acid and orange peel activated with potassium carbonate, but the study was carried out using orange peel activated with potassium carbonate because the adsorption capacity of orange peel activated with potassium carbonate is higher than that of both original orange peel and orange peel activated with phosphoric acid. This is an evidence that orange peel was activated with potassium carbonate. The effect of adsorbent amount, contact time, pH, and temperature on the adsorption rate of Cr(III) ions was investigated.

MATERIALS AND METHODS

Apparatus

An ATI UNICAM 939 model flame atomic absorption spectrophotometer (FAAS), equipped with a deuterium lamp, was used for the determination of Cr(III). To measure pH the solutions, a pH meter (Mettler Toledo Model) was used.

Materials

In this study, orange peel, which is one of the food industry wastes, activated with potassium carbonate was used as the adsorbent. 1000 mg/L of Cr(III) stock solutions was prepared from $Cr(NO_3)_3{\cdot}9H_2O$ (Merck). All chemicals were of analytical reagent grade and deionized water (Model: Expe-UP Series, PURIS, 0.05 µS/cm) was used for the preparation of all solutions. All glass vessels were cleaned before usage by soaking them in 5% HNO_3 and then rinsed thoroughly with deionized water.

Preparation of Adsorbent

The orange peel was obtained from oranges grown in the Mediterranean Region (Turkey) and sold in the local market (Burdur) as Finike Orange. The orange peels were washed with water to remove water-soluble contaminants and passed 4 times through ultrapure water. After washing, the orange peel was dried at 323 K in the oven. Then, the dried samples are ground to obtain the powdered sample. Afterwards, 50 g of the ground orange peel was put into 500 mL of 0.10 mol/L potassium carbonate solution at the room temperatures and allowed to stand for 24 hours with stirring. Then, the activated orange peel is filtered and washed with ultrapure water. The washing process was repeated until pH value of the wash water was about 7. The residue was then dried at 323 K for 24 hours in the oven. The resulting obtained adsorbent (OPAPC) was stored in a polyethylene container for using at further experiment. The BET (Brunauer-Emmett-Teller) surface area was found as 1.53 m^2/g using N_2-adsorption isotherm data at the relative pressure (P/P_0) values of between 0.05 and 0.031.

Adsorption Experiments

The adsorption of Cr(III) ions was carried out a constant mixing speed (500 rpm) in a batch adsorption system. The chromium solutions were obtained from a stock Cr(III) solution (1000 mg/L). The effects of parameters such as OPAPC amount, contact time, pH, and temperature on Cr(III) adsorption were investigated. The effect of the amount of OPAPC on adsorption was investigated using 20 mL of 20 mg/L Cr(III) solutions at a range of between 2 and 15 g/L OPAPC. To examine the effect of contact time on adsorption process, 150 mL of 10-50 mg/L Cr(III) solution and 1.2 g of OPAPC were used at between 10 and 240 min intervals. The effect of pH on adsorption was investigated between 3 and 7 and the effect of temperature was investigated at 298, 308 and 318 K using 20 mL of 30 mg/L Cr(III) solution. The amounts of Cr(III) remaining in the solution after adsorption were determined by FAAS instrument. The percentage of adsorption and adsorption capacity (q_e, mg/g) were calculated using the following equations:

$$Adsorption(\%) = \frac{(C_0 - C_e)}{C_0} * 100 \quad \text{(Eq. 1)}$$

$$q_e = \frac{(C_0 - C_e) * V}{m} \quad \text{(Eq. 2)}$$

where, C_0 (mg/L) and C_e (mg/L) are chromium intial and final concentrations, respectively, V(L) is the volume of solution, and m(g) is the mass of adsorbent.

RESULTS AND DISCUSSION

Effect of adsorbent amount

The amount of adsorbent is a crucial factor to determine the metal removal potential for any concentration at any matrix. The effect of OPAPC amount on the adsorption of chromium was investigated by using 20 mL of 20 mg/L chromium solution with 2-15 g/L of adsorbent amount. The results are shown in Figure 1. By the time OPAPC amount increased, the removal of Cr(III) was also increased and it was observed that the highest adsorption efficiency was reached using 8 g/L of OPAPC adsorbent amount. Furthermore, the increase in the efficiency of adsorption was not significantly changed when the adsorbent amount was higher than 8 g/L value. For this reason, further experimental work was carried out with an amount of 8 g/L value of adsorbent. The adsorption efficiency is increased because of the fact that the active surface suitable for adsorption is increased at higher adsorbent amount (16). On the other hand, the significant increase in adsorption yield after a certain amount (8 g/L) of adsorbent was not observed because of the fact that most of the metal ions in solution were adsorbed at the value of 8 g/L of adsorbent amount. As a result, the increase in adsorption yield in the amounts of OPAPC above 8 g/L is insignificant.

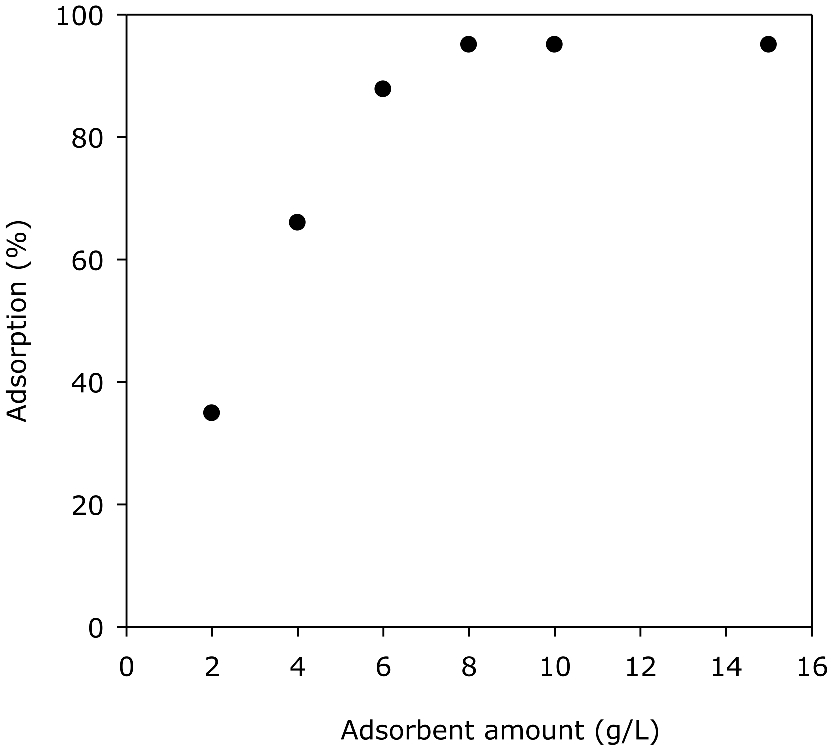

Figure 1: Effect of adsorbent amount on Cr(III) adsorption (Cr(III): 20 mg/L, contact time 240 min, pH 3, T= 298 K).

Effect of pH

pH is one of the most crucial parameters affecting adsorption as both the solubility of metal ions and total charge of the adsorbent. In addition, the acidity of the environment also affects the ability to compete for hydrogen ions and metal ions on available centers of the adsorbent surface. The effect of pH on the adsorption of Cr(III) on potassium carbonate activated orange peel was investigated in solutions containing 20 mL of 30 mg/L Cr(III) in the pH range of between 3 and 7 at 298 K. The results are shown in Figure 2. The effect of the pH on the adsorption was investigated in the range between 3 and 7 because the pH value of the real sample solution in the nature is around 3 or more, and the precipitation of metal ions with hydroxide ions generally occurs after pH 7. As seen in Figure 2, the highest adsorption yield was achieved at a value of about pH 3. Additionally, the adsorption efficiency is decreased by the increasing the pH value. It is also important that the pH adjustment is not needed since the acidity of the prepared solution is about pH 3. Lyubchik *et al.* (17) found the highest adsorption yield when the pH of solution was between 2 and 3 for the adsorption of Cr(III) ions on the commercial activated carbons. According to these results, the reason of maximal adsorption (pH of 2–3.2) is that the carbon’s surface has different affinities to the different chromium species in the solution, and the pH of the solution strongly affects the affinity of the chromium ions. Ugbe *et al.* investigated the effect of pH of 2, 4, 7, 9, and 12 to obtain maximum adsorption of Cr(III) ions from aqueous solution using orange peel as adsorbent and the results revealed that the optimum adsorption was obtained at pH 2 at constant 303 K. The reason is that in aqueous solution Cr(III) is oxidized to CrO_4^{2-} form and this negatively charged form is able to be adsorbed by the protonated groups present on the surface of adsorbent at low pH values (18).

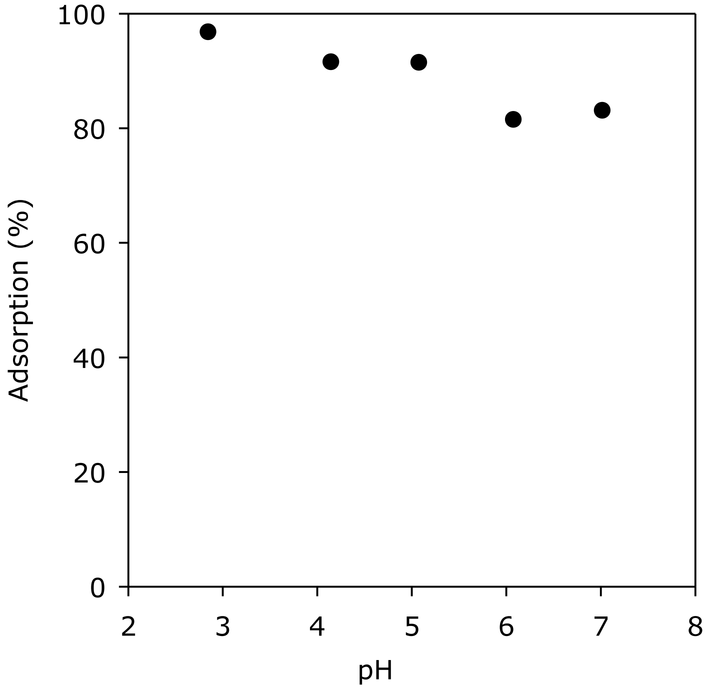

Figure 2: pH effect of Cr(III) adsorption (Cr(III): 30 mg/L, T= 298 K, adsorbent amount= 8 g/L, contact time = 60 min).

Effect of temperature

The effect of temperature on the removal of Cr(III) ions was investigated between 298 and 318 K by keeping the other experimental conditions constant. The results are shown in Figure 3. As seen in the figure, the adsorption efficiency decreased with increasing temperature. This result may be due to the fact that the adsorption process of Cr(III) ions is exothermic. ΔG , ΔH , and ΔS for adsorption were calculated using equations below (19, 20).

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad \text{(Eq. 3)}$$

$$\Delta G = \Delta H - T\Delta S \quad \text{(Eq. 4)}$$

Where, *R* (8.314 J/mol K) is the gas constant, *T* (K) is the absolute temperature and *K*d (dm^3/g) is the distribution coefficient defined as $\frac{q_e}{C_e}$. A graph of lnK_d versus $\frac{1}{T}$, *ΔH* and *ΔS* were determined from the slope and intercept of the plot, respectively. The *ΔH* and *ΔS* of adsorption onto OPAPC were respectively -18.78 kJ/mol and -0.052 kJ/mol K. Negative values of *ΔH* and *ΔS* indicated that Cr(III) adsorption was an exothermic process and the irregularity decreases during Cr(III) adsorption. *ΔG* of Cr(III) adsorption onto OPAPC was -3.24, -3.26 and -2.18 kJ/mol at 298, 308, and 318 K, respectively. It shows that the adsorption of Cr(III) onto OPAPC is physical because of the fact that the *ΔG* values for physisorption is changed between -20 and 0 kJ/mol but that of chemisorption is changed between -80 and -400 kJ/mol (18, 21). These results revealed that the adsorption of Cr(III) onto OPAPC was thermodynamically feasible and could occur spontaneously.

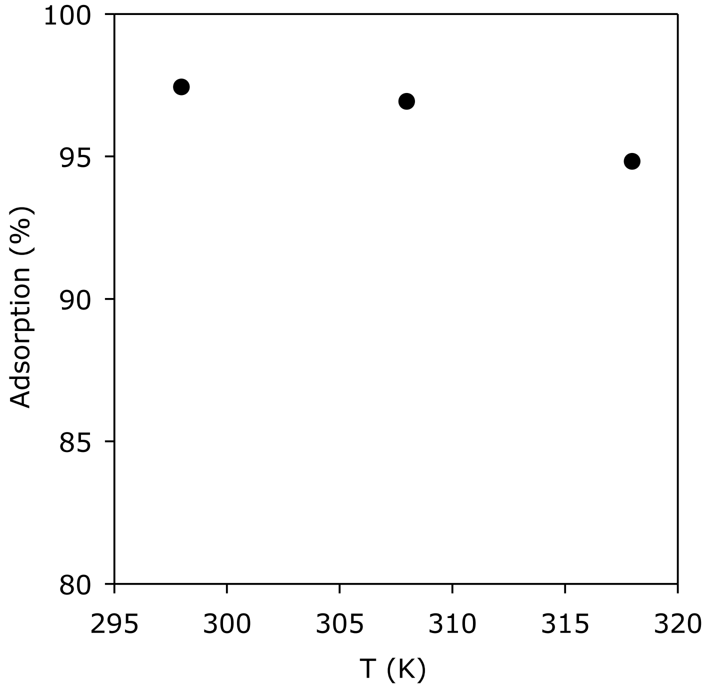

Figure 3: The effect of temperature on Cr(III) adsorption (Cr (III): 30 mg/L, pH= 3, adsorbent amount= 8 g/L, contact time= 60 min).

Effect of Contact Time and Adsorption Kinetics

Since the adsorption is a time dependent process, it is important to determine the adsorption rate in process design. For this reason, the influence of the contact time of Cr(III) ions on adsorption with OPAPC was investigated at different chromium ion initial concentrations to determine the equilibrium time to maximally remove Cr(III) ions and the kinetics of the adsorption process. The results are shown in Figure 4. Under working the experimental conditions, Cr(III) ions greater than 80% in solution are removed within 10 min and the equilibrium is reached within 60 min. The increase in the efficiency of adsorption does not appear to be significant during contact times after 60 min. For this reason, the 60 min contact period was defined as the equilibrium time. This result shows that a longer contact is not a practical matter since the adsorbent surface becomes saturated with Cr(III) ions under equilibrium conditions.

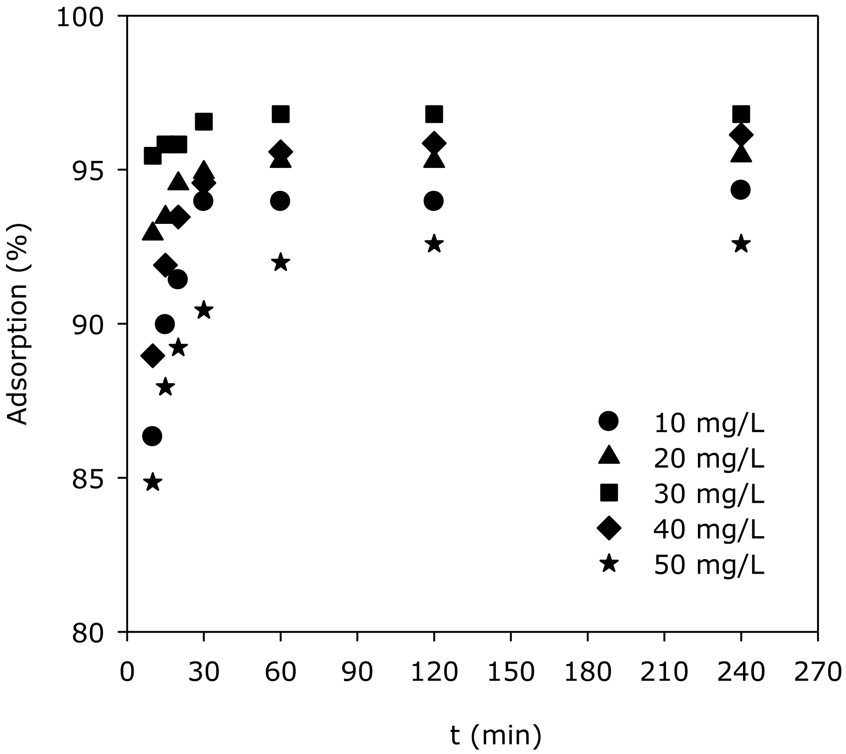

Figure 4: Effect of contact time for Cr(III) adsorption (Cr(III): 30 mg/L, pH= 3, adsorbent amount= 8 g/L, T= 298 K).

Adsorption rate gives crucial information for the design of the adsorption systems. The kinetics of pollutant removal is required to determine optimum conditions. Pseudo-first order and pseudo-second order kinetic models were used to determine the rate of adsorption of Cr(III) ions by OPAPC adsorbent. The first-order kinetic model assumes that the metal ion is bound only to an area of the sorbent surface of the adsorbent. In this model, the adsorption rate is proportional to the number of free active sites and the model is expressed by the following equation (22, 23).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad \text{(Eq. 6)}$$

where, k_1 (min^{-1}) is the so-called first-order adsorption rate constant. q_e and q_t are the amount of adsorbed material per unit mass of the adsorbent at equilibrium and at any instance (t). The values of k_1 and q_e are calculated from the slope and slope of the line obtained by plotting $\ln(q_e - q_t)$ against time (t).

The second order kinetic model assumes that the chemical interactions leading to the binding of metal ions to the surface by means of strong bonds as strong as the covalent bond determine the rate of the reaction. The pseudo-second-order model is expressed by the following equation.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad \text{(Eq. 7)}$$

Where, k_2 (g/mg min) is the second order adsorption rate constant. Plots of (t/q_t) versus (t) give the values of $1/q_e$ as the slope and $1/ k_2q_e^2$ as the intercept. The suitability of the kinetic models to the experimental data can be determined by the correlation coefficient (R^2) and the calculated q_e values. The model approaches R^2 value to 1 and close to the calculated q_e value of the experimental q_e value is accepted as the most compatible model. The obtained kinetic parameters are given in Table 1. When Table 1 is examined, as the correlation coefficients obtained from the kinetic equations are higher for the quadratic equation, the adsorption of Cr(III) ions is suitable for the second order kinetic model. Moreover, the theoretical q_e values calculated from the model equations are very close to the experimental (q_e, exp.) values. This indicates that the obtained experimental data is more suitable for the second order kinetic model. According to these results, it can be said that the adsorption process between OPAPC adsorbent and Cr(III) ions is in the second order.

Table 1: Kinetic parameters for the adsorption of Cr(III) on OPAPC at 298 K.

Cr(III) mg/L	$q_{e\text{-exp.}}$	Pseudo-first order			Pseudo-second order		
		q_e	k_1	R^2	q_e	k_2	R^2
10	1.181	0.485	0.149	0.966	1.182	1.332	1.000
20	2.389	0.138	0.084	0.954	2.389	1.645	1.000
30	3.626	0.052	0.033	0.946	3.632	2.059	1.000
40	4.784	0.028	0.092	0.984	4.822	0.308	1.000
50	5.787	0.800	0.062	0.919	5.811	0.215	1.000

Effect of initial concentration and adsorption isotherms

The initial concentration of the metal ions is crucial to overcome the mass transfer resistor between aqueous and solid phases (7). As the initial concentration of metal ions in the solution increases, the adsorption capacity increases and the metal removal efficiency decreases with the increase of the metal ion initial concentration. Increasing the initial metal concentration leads to an increase in the adsorption capacity which provides a driving force between the adsorbent and the adsorption medium to overcome the mass transfer resistor. The removal of ions by the adsorbent increases with increasing initial ion concentration. In the low ion concentration in the solution, the ions interact with the binding sites and thus, almost 100% of adsorption can take place. However, at higher concentrations, more ions may remain in the solution medium without being adsorbed due to saturation of the binding sites.

The effect of initial concentration on the adsorption capacity of Cr(III) ions with OPAPC adsorbent is shown in Figure 5. When Figure 5 is examined, the amount of Cr(III) ions adsorbed per gram of adsorbent (q_e) is increased by the increase of the concentration of Cr(III) ions. By increasing the initial concentration of Cr(III), C_o, ions from 5 mg/L to 50 mg/L, the amount of Cr(III) ions adsorbed per gram of adsorbent increases from 0.579 mg/g to 5.77 mg/g. These results show that the adsorption depends on the initial concentration.

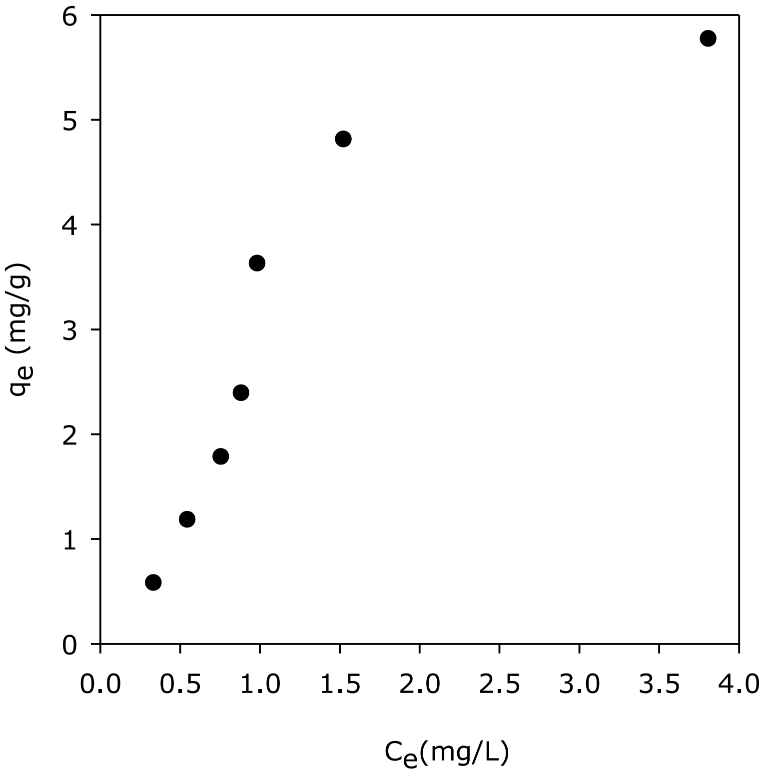

Figure 5: Effect of initial concentration of Cr (III) ions on adsorption capacity (pH 3, adsorbent amount= 8 g/L, T= 298 K).

Adsorption isotherms are used to explain the relationship between the amount of adsorbed material on the adsorbent and the amount of dissolved material in the liquid. Two- or three-parameter models have been developed to explain the experimental results of adsorption isotherms. The most commonly used parameters are Langmuir and Freundlich isotherm models, respectively. While the Langmuir model is based on the assumption of a completely homogeneous adsorption surface, the Freundlich model is valid for heterogeneous surfaces. Langmuir and Freundlich isotherms are expressed by the following equations (12, 24).

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad \text{(Eq. 8)}$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad \text{(Eq. 9)}$$

q_m (mg/g) and K_L in the Langmuir isotherm equation are the isotherm constants which express the maximum adsorption capacity and binding energy, respectively. Plots of C_e versus $\frac{C_e}{q_e}$ give the values of $\frac{1}{q_m}$ as the slope and $\frac{1}{K_L q_m}$ as the intercept. The K_F and n values in the Freundlich isotherm equation are Freundlich isothermic constants giving information on adsorption capacity and adsorption yield, respectively. The direct K_F and n values obtained from the log(q_e) values plotted against the log(C_e) values in the linearized form of the Freundlich equation can be calculated.

In this work, the adsorption of Cr(III) with OPAPC adsorbent was modeled using Langmuir and Freundlich isotherms. Experimental data showed that the adsorption was compatible with the Freundlich isotherm. The K_F and n values were 2.36 and 1.03, respectively. Since n is in the range of 1 to 10, the adsorption is convenient. The compatibility of the experimental data with the Freundlich isotherm model suggests that the adsorption takes place on a heterogeneous solid surface. Guiza has reported that Freundlich isotherm model was performed on copper adsorption using the original orange peel (25). On the other hand, Marín *et al.* has reported that the adsorption capacity of Cr(III) ions using orange waste was higher than that of activated with formaldehyde, methanol, and acetic acid and this adsorption was described as Langmuir isothermic model (26). In another study, the adsorption of Cr(III) ions using orange peel activated with formaldehyde was convenient by Langmuir isotherm model (27).

CONCLUSION

Cr(III) removal from the aqueous solutions with the orange peel activated with potassium carbonate (OPAPC) used as adsorbent was successfully carried out. As the adsorbent amount was increased for Cr(III) removal, the adsorption efficiency was also increased but no significant increase was observed after the adsorbent amount of 8 g/L. It was determined that the adsorption efficiency was dependent on pH and the highest adsorption efficiency was reached at about pH 3 which is also an original pH value of the prepared solution in this study. A decrease in adsorption efficiency was observed with an increase of temperature. In addition, adsorption studies have shown that a greater than 80% of the Cr(III) ions are removed within the first 10 min and the equilibrium is reached in 60 min, the adsorption rate is defined by a pseudo second order kinetic model. The results have shown that the orange peel activated with potassium carbonate (OPAPC) can be used as an effective adsorbent to remove chromium ions from the water.

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