DETERMINATION OF REMOVAL EFFICIENCY OF HEXAVALENT CHROMIUM FROM AQUEOUS SOLUTIONS AND TANNERY WASTEWATER USING KAOLINITE

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ABSTRACT

The discharge of effluents containing chromium (VI) generated by tannery industry reveals serious toxicological and aesthetical problems in the environment. In this study, the use of kaolinite as an adsorbent was evaluated in the tannery wastewater treatment. The sorption of Cr(VI) from aqueous solution and tannery wastewater was conducted by a batch technique. Furthermore, systematic zeta potential experiments have been performed to be able to understand the adsorption mechanism and process. Consequently, zeta potential of kaolinite was not dramatically varied with the solid concentration, but pH altered the zeta potential of the suspensions. After the investigation of variation of zeta potential for kaolinite suspensions, isoelectric point was determined at about pH 2.15. For adsorption process, increase in pH was resulted the adsorption in the direction of decrease, and increase in temperature and ionic strength was not changed significantly the adsorption of hexavalent chromium. The results indicate that kaolinite could be employed as a low cost adsorbent for removals of Cr(VI) from aqueous solutions including industrial wastewaters.

KEYWORDS:
Chromium (VI) removal; kaolinite; adsorption; zeta potential; tannery wastewater.

INTRODUCTION

Increasing industrialization and technological development during the last century has resulted in severe metal pollution of the environment. Heavy metals such as chromium (Cr), cadmium (Cd), lead (Pb), copper (Cu), nickel (Ni), and mercury (Hg) are nowadays among the most important pollutants in aquatic environments [1]. Water pollution by heavy metals, especially chromium has sparked much concern to societies and regulation authorities around the world [2]. Chromium in aquatic environments are mainly generated from various industrial processes such as electroplating, metal finishing, leather tanning, wood preserving and manufacturing of dyes and paints [3]. Among them, tannery industry is one of the most polluting industries and characterized by considerable water consumption associated with the large use of different chemicals. The function of chromium salts in tanning processes is to form through complexation with the polypeptide collagen components of leather, a protective layer, which prevents the penetration of water inside the leather pores avoiding putrefaction. [4].

Chromium exists in the environment in the trivalent state, i.e. in the cationic form as Cr(III), or in the hexavalent state as the Cr(VI) anions: $HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$. Cr(VI) is toxic to both plants and animals. As a strong oxidizing agent and a potential carcinogen it can have teratogenic and mutagenic effects. Concentrations as low as 0.5 ppm in solution and 5 ppm in soil can be toxic to plants [5,6]. Cr(VI) is approximately 100 times more toxic [7] and 1000 times more mutagenic than Cr(III) [8], which is known to be indispensable for animal nutrition. Besides, Cr(VI) is very toxic to living organisms, being its toxicity due to its high redox potential, mobility and ability to penetrate biological membranes. Cr(III) is less toxic and acts as essential micro element in mammalians, but in plants its role has not been elucidated yet [1]. Exposure to Cr(VI) causes irritation and corrosion of skin, respiratory tract, and probably lung carcinoma. Epigastric pain, nausea, vomiting, severe diarrhea, and hemorrhea are other deadly consequences of Cr(VI) contamination. The International Agency for Research on Cancer (IARC) has classified inhaled Cr(VI) as a human carcinogen [9]. In order to minimize these health risks, the maximum permissible level of Cr(VI) in industrial wastewater is recomended as 0.5 mg/L based on the national regulations of water pollution control in Turkey. According to the recommendation of the World Health Organization (WHO), the maximum allowable limit for Cr(VI) in drinking water is at the level of 0.05 mg/L [10].

Although numerous methods exist, the most commonly used methods for removing Cr(VI) from wastewater include reduction [11,12], precipitation

[13], membrane filtration [14,15], biological method [16], ion exchange [17-20] and adsorption [21–25]. The first five conventional separation methods have many disadvantages for instance, the high capital and operational cost, the production of amount of chromium sludge and possible generation of secondary pollution resulting in high disposal costs [26], whereas adsorption has been widely used in the removal of Cr(VI) from wastewater due to its simple operation, high removal efficiency and low treatment cost. Various materials such as modified zeolite and zero valent iron, clay minerals, waste tyres, activated carbon, biomaterials and industrial wastes have been used as adsorbents for the removal of chromium. Kaolinite is an inexpensive and efficient adsorbent which has great potential in the application of heavy metal removal from wastewaters because of its abundance, chemical and mechanical stability, high adsorption capability and unique structural property. Removal of metal ions using kaolinite is based on ion exchange and adsorption mechanisms because of its relatively high cation exchange capacity (CEC) (15–75 mmol/<<kg) and specific surface area, ranging from 10 to 20 m^2/g. In recent years, many studies have been conducted on the adsorption of hazardous substances such as heavy metals and organic pollutants by kaolinite [27]. However, the applications of kaolinite for removal of Cr(VI) are limited.

In the present work, adsorptive removal of Cr(VI) from aqueous solution and tannery wastewater sample was studied using kaolinite under various environmental conditions. After the determination of zeta potential of kaolinite, the effects of experimental conditions on the removal efficiency of the hazardous chromium including pH, temperature and ionic strength were studied.

MATERIALS AND METHODS

Materials. Analytical grade chemicals were used throughout the investigation. Merck salts and standards used for quantification were of high purity (99.9% or above). Stock and test solutions of chromium were prepared from K_2CrO_4. Sample of tannery wastewater containing chromium was collected from a local leather industry situated at Gönen, Balıkesir, in a big plastic bottle of 5 L capacity. The color of collected sample was greenish blue, its pH value was 4.5±0.1. The testing samples contained Cr(VI) 6.90 mg/L. The kaolinite was obtanied from Sigma Aldrich and average size of the adsorbent was found to be around 3 μm.

Characterization. The pH of the solution was adjusted with a Hanna pH-meter. The shaking was carried out in an orbital shaker incubator. The centrifugation was done with a Nuve centrifuge machine at 3000 rpm. Chromium content of the samples were determined spectrophotometrically using Perkin Elmer UV/Vis Spectrophotometer.

Method. The sorption of Cr(VI) on kaolinite was studied by a batch technique. Ultrapure water was used in all experiments. All the solutions were stored in polyethlene bottles. Aqueous standard solutions of Cr(VI) were prepared by dissolving an accurately weighed amount of the relevant salt in deionized water so as to yield a metal ion concentration of 1000 mg/L. Adequate aliquots were taken from this stock for subsequent dilution to the desired concentration level. Adsorption experiments were carried out in polyethylene flasks of 50 mL using 0.5 g kaolinite and chromium ions in the range of 5 to 400 mg/L. pH of solutions was fixed up with 0.1 N HCl and 0.1 N NaOH without adding any buffer to control the pH. The flasks containing the weighed amounts of kaolinite and chromium solution were kept seperately in the incubator before mixing for a sufficient period of time to attain the desired experimental temperature. The equilibration time was run for 24 h. Samples were withdrawn and the supernatant of the solution was separated by centrifuging at 3000 rpm for 4 min. Centrifugation was performed to deport kaolinite from aqueous medium. The filtrate was analyzed for the residual Cr(VI) concentration using UV-visible spectrophotometer at the maximum wavelength (λ_{max}=378 nm) of the adsorbate. The adsorption capacity, qe, was calculated from the difference between the initial and equilibrium concentrations of Cr(VI). The effects of pH, ionic strength and temperature on the adsorption capacity of kaolinite were investigated.

Determination of Zeta Potential of Kaolinite. A bunch of experiments were implemented to be able to determine the isoelectric point of the adsorbent. The measurements were carried out as a function of firstly the solid concentration and then pH of the suspensions. After the suitable solid concentration was determined, a sample of 0.4 g kaolinite was transferred to 100 mL distilled water of the adjusted pH. The ultrasonic vibration of dispersion was enforced for 10 min, shortly after settled in an incubator and rinsed for 24 h at 25±2 ºC. Afterwards, these samples were set free to stand for 15 min to let larger particles stable. An aliquot taken from the supernatant was used to measure the zeta potential using a Nano-zetasizer instrument (Malvern Co.) at room temperature.

Effect of initial pH on adsorption. The effect of pH on the sorption capacity of adsorbate (Cr(VI)) onto kaolinite was examined in the pH ranges of 2.5-5.5. The pH of each solution was

adjusted using required quantity of HCl and NaOH solutions before the adsorption experiments.

Effect of temperature. Adsorption experiments were carried out under batch mode at 30, 40, 50 and 60 ºC temperature. Temperature values of the solutions was kept stable using an orbital shaker incubator.

Effect of ionic strength on adsorption. Ionic strength of chromium solutions was adjusted using NaCl salt in the concentrations of 0, 0.01, 0.05 and 0.1 molL^{-1}.

RESULTS AND DISCUSSION

Zeta Potential of Kaolinite Suspensions. The pH$_{PZC}$ is defined as the pH at which charge transition of surface occurs. At this pH, the actual charge on the adsorbent surface is zero. The pH$_{PZC}$ is a very important parameter as the charge on adsorbent surface determines attraction or repulsion of adsorbate. If adsorbent surface is positively charged (initial pH <pH$_{PZC}$) then it attracts negative species and when it is negatively charged (initial pH > pH$_{PZC}$), it tends to attract positive species [28-30]. For silicate and alumina type minerals potential determining ions are generally H$^+$ and OH$^-$ ions. In addition, the H$^+$ ions in solution undergo exchange with some of the cations in the solid lattice leading to the consumption of H$^+$ ions in suspension [31]. First of all the solid concentration in solution is a main parameter related with the surface charge generation. This means that the ionic species produced at the solid-liquid interface increase with increase in solid concentration that using inadequate solid concentrations can lead to errors in the interpretation of zeta potential measurements. The variation of the zeta potential with solid concentration of kaolinite suspensions has been shown in Fig.1.

This figure shows that the zeta potential of kaolinite suspensions was not dramatically changed with solid concentration. Fig.2 illustrates the effect of pH on zeta potential of kaolinite. As shown in this figure, kaolinite has an IEP at about pH 2.15 and exhibits negative zeta potential value over pH 2.15. In the literature the IEP of kaolinite varies considerably depending on the source of the sample and the procedure used for cleaning the surface prior to study [32]. The increase of the suspension pH results in an increase in the negative charge of kaolinite. This can be ascribed to either the adsorption of OH$^-$ ions onto the positive charge centers of kaolinite or the deprotonation of surface hydroxyl groups. In addition, the reaction of OH$^-$ with dissolved cations to form metal hydroxides may result in a decrease in the pH. The decrease of the suspension pH results in a decrease of the negative potential owing to the H$^+$ adsorption on the negative charge centers. At around pH 2.15, the zeta potential is about 0 mV. Most silicate or clay minerals have the isoelectrical point in the pH range of 2 to 4 [33].
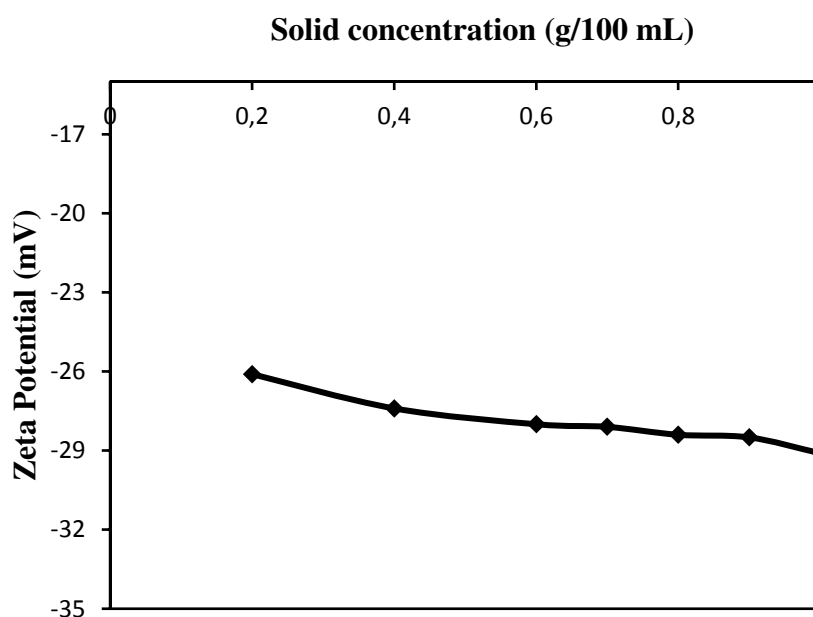

FIGURE 1
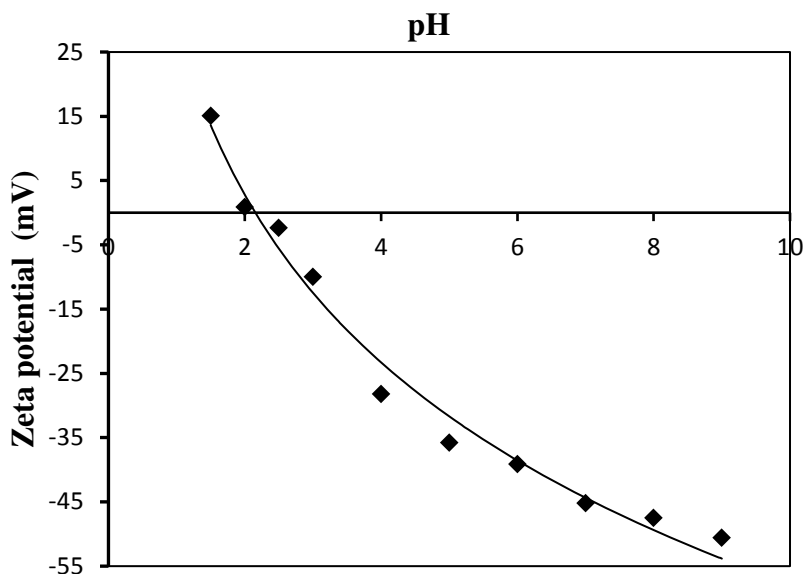**The variation of zeta potential with solid concentration of kaolinite suspensions.**

FIGURE 2
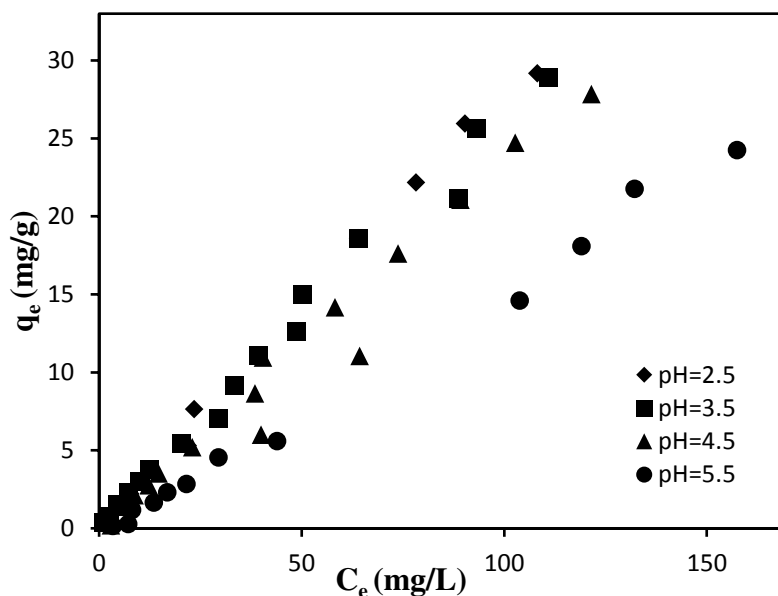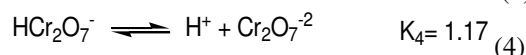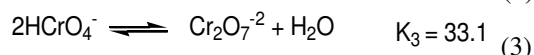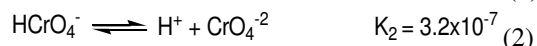**The variation of zeta potential with pH of kaolinite suspensions.**
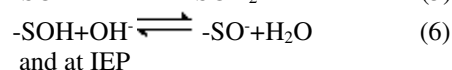

FIGURE 3
The variation of Cr(VI) adsorption with pH on kaolinite

Effect of Initial pH on Adsorption. The pH plays an important role in the adsorption behavior because the pH can have an effect not only on the surface charge density of the adsorbent but also on the existing form of the adsorbate [2]. Therefore, aqueous phase equilibrium concentrations of chromium species can be evaluated using appropriate chemical reaction equilibrium analyses to understand the distribution of various forms of chromium (VI) ions in solution. In aqueous solution, Cr(VI) exists in different ionic forms dependent on both total Cr(VI) concentration and pH. Cr(VI) exists in five main forms in aqueous solution, and the equilibrium reactions for different Cr(VI) species are shown in Eqs. 1-4 as follows [34]:

$$H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^- \qquad K_1 = 0.16 \quad (1)$$

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{-2} \qquad K_2 = 3.2 \times 10^{-7} \quad (2)$$

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{-2} + H_2O \qquad K_3 = 33.1 \quad (3)$$

$$HCr_2O_7^- \rightleftharpoons H^+ + Cr_2O_7^{-2} \qquad K_4 = 1.17 \quad (4)$$

The other two forms of Cr(VI), $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$, have been reported to exist at concentrations higher than 0.1 mol/L, and their concentrations are too low to be considered under the experimental conditions [34]. Figure 3 represents the removal of chromium (VI) with respect to the different initial pH values in the range of 2.5 to 5.5 on kaolinite and shows that adsorption capacity decreases with increase in pH.

As seen from the figure, the initial pH value of Cr(VI) solution had a strong effect on the adsorption behavior of kaolinite [34]. The results show that chromium removal increases with decrease in pH values. Additionally, it can be drawn a conclusion from the Figs.4 and 5 that chromium removal efficiency of the wastewater decrease with increase in pH. In Figure 2, kaolinite surface in water had a net negative surface charge at natural pH and the isoelectrical point of kaolinite was at about pH 2.15. The electrical charge at the oxide surface /aqueous phase to protonation/deprotonation of the surface hydroxyl can be ascribed as [5]:

$$-SOH + H^+ \rightleftharpoons -SOH_2^+ \qquad (5)$$

$$-SOH + OH^- \rightleftharpoons -SO^- + H_2O \qquad (6)$$

and at IEP

$$[-SOH_2^+] = [-SO^-] \qquad (7)$$

The fact that kaolinite has an isoelectric point shows the reaction responsible for the surface charge of the solid is mainly the reaction in Eq. (5) below IEP and in Eq. (6) above IEP, respectively. At lower pH the surface of the adsorbent was more protonated and competitive negative ions
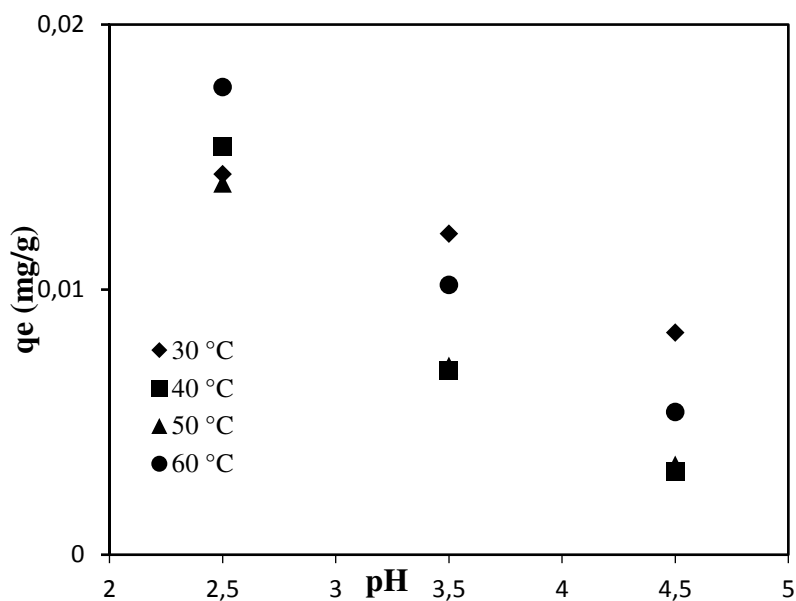

FIGURE 4
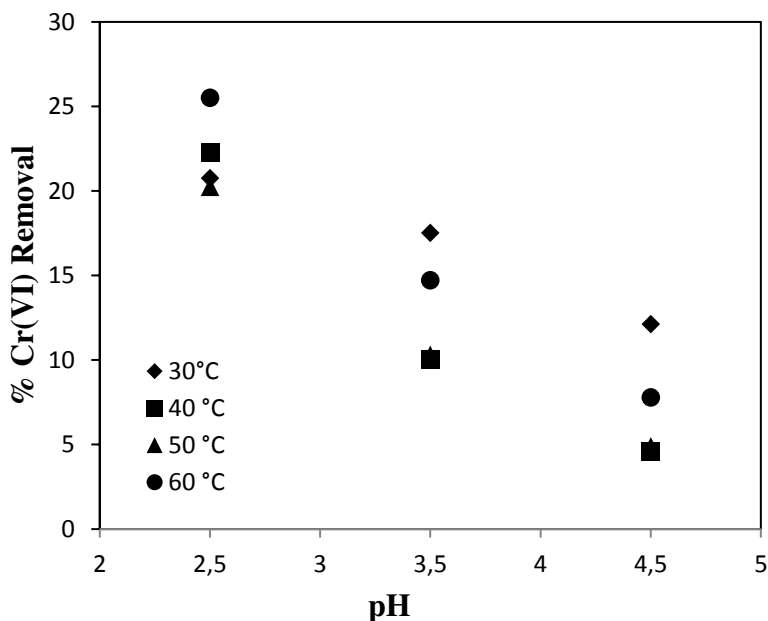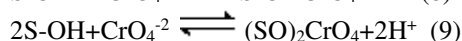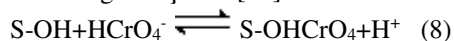**Effect of initial pH of the wastewater on Cr(VI) adsorption by kaolinite.**

FIGURE 5
Effect of initial pH of the wastewater on % Cr(VI) removal efficiency.

adsorption occurred between positive surface ($-OH_2^+$) and free chromate ion. Adsorption of Cr(VI) at pH 2.5 shows the bind of the negatively charged chromium species ($HCrO_4^-$) occurred through electrostatic attraction to the positively charged (due to more H^+ ions) surface functional groups of the adsorbent [35]. At the initial concentration of 100 mg/L and pH range from 2.5 to 5.5, $HCrO_4^-$ was the dominant Cr(VI) species [34]. However, at higher pH above 5.0, the amount of CrO_4^{2-} increases, which is not adsorbed by the adsorbent, leading to a decrease of the adsorption capacity. In addition, with increasing in pH values due to more OH^- ions, the protonation ability of the functional groups was weakened and the adsorption capacity declined [2,35].

The adsorption reactions of Cr(VI) on kaolinite from aqueous solutions can be given as following in Eqs 8-9 [34].

$$\text{S-OH} + \text{HCrO}_4^- \rightleftharpoons \text{S-OHCrO}_4 + \text{H}^+ \quad (8)$$

$$\text{2S-OH} + \text{CrO}_4^{-2} \rightleftharpoons (\text{SO})_2\text{CrO}_4 + 2\text{H}^+ \quad (9)$$

Effect of Temperature on Adsorption. The effect of temperature on adsorption is important not only because it affects the rate and extent of adsorption but also due to the fact that temperature dependence of adsorption provides information about possible adsorbate-adsorbent interaction [36]. In the temperature range of 30–60 ∘C, the adsorption capacity of kaolinite for chromium (VI) was determined. It can be seen from Fig.6 that temperature has not an important effect on adsorption. Figs.4-6 indicate that the adsorption slightly decreased with increase of the solution temperature. This shows that the adsorption process is an exothermic process. An increasing adsorption temperature leads to increasing of particle movements at the surface of the adsorbent and this phenomenon facilitates the detachment of Cr(VI) from the adsorbent [37]. This confirms the exothermic nature of Cr(VI) adsorption onto kaolinite [38,39].

Effect of Ionic Strength on Adsorption. Investigations carried out on adsorption revealed that the extent of waste uptake was strongly influenced by the concentration and nature of the electrolyte ionic species added to the aqueous media [40]. Industrial wastewaters often contain a variety of different ions [27]. In this study, NaCl was chosen as a salt for investigating the effect of ionic strength to the adsorption of Cr(VI) on kaolinite. To
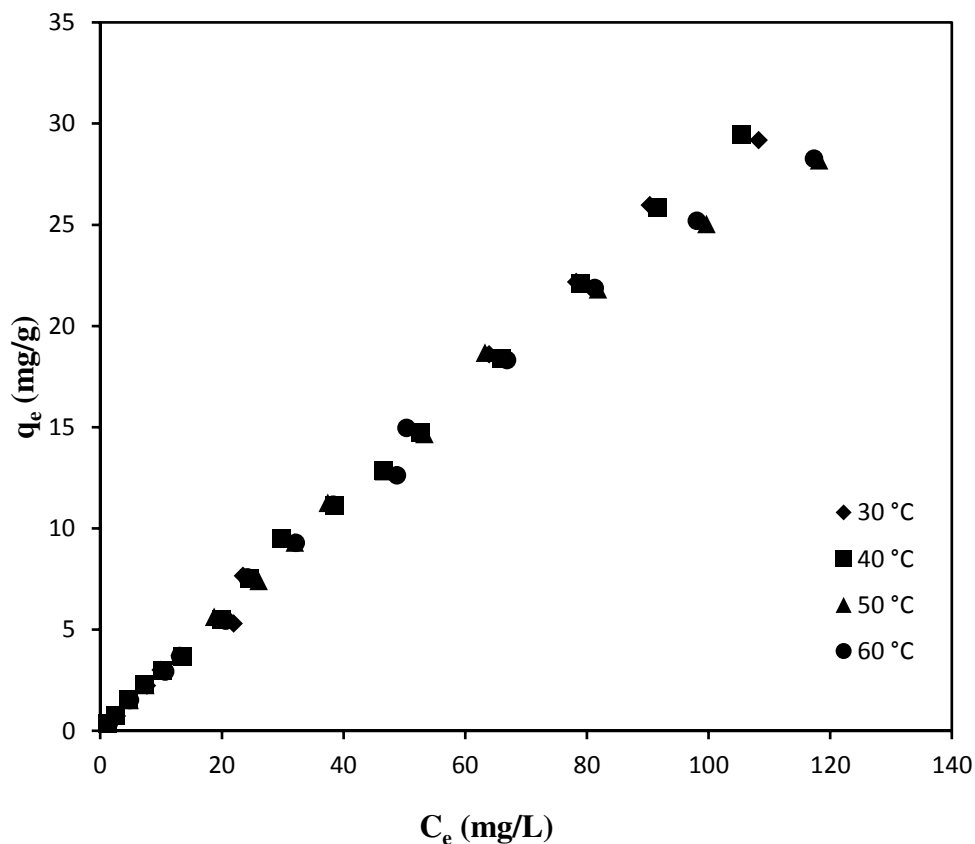

FIGURE 6
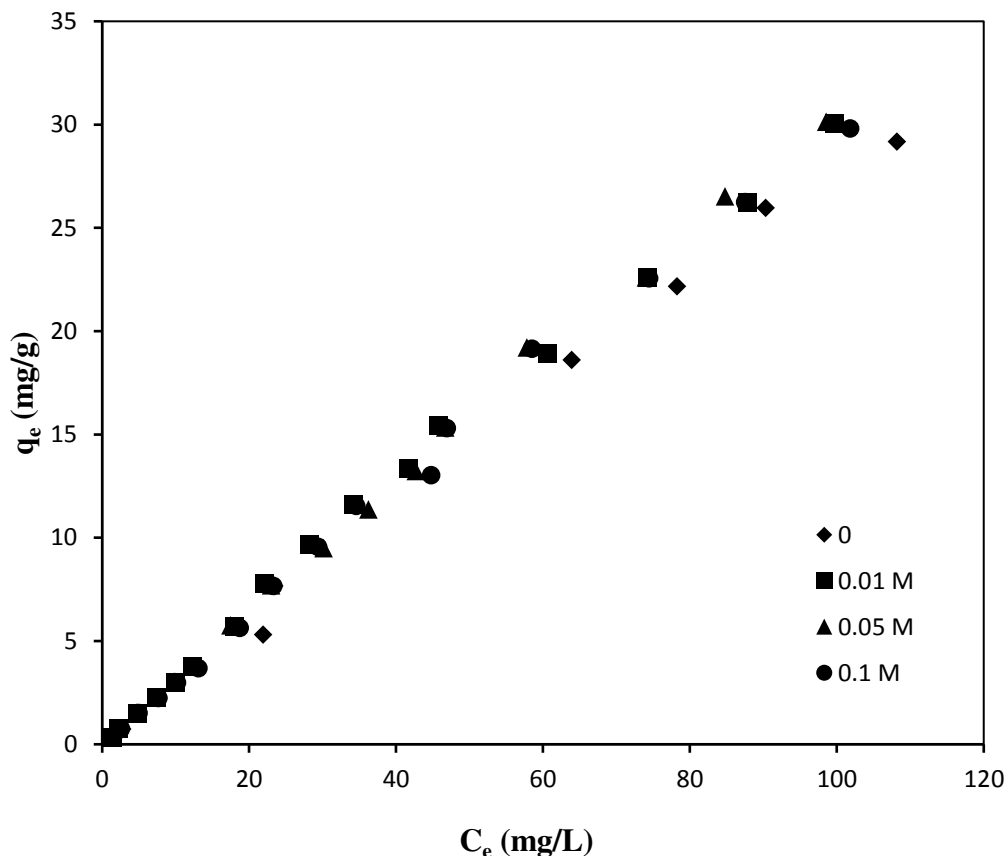**The variation of Cr(VI) adsorption on kaolinite with temperature**

FIGURE 7
The variation of Cr(VI) adsorption with ionic strength on kaolinite.

check the effects of electrolyte composition on the adsorption, ionic strengths of 0.01, 0,05 and 0.1 mol/L NaCl were used to test whether ionic strength affected the adsorption of Cr(VI) on kaolinite with an initial Cr(VI) concentrations ranging from 10 to 250 mg/L [27]. Figure 7 shows the effect of the ionic strength on the Cr(VI) adsorption capacity [2].

Results clearly depict that the adsorbed amount was slightly higher in the presence of salt [5]. Since the presence of NaCl in the solution enhances the electrostatic interaction of similar charges of the kaolinite surface and Cr(VI), the adsorbed amount should increase with increase of NaCl concentration [41]. Similar results found that the presence of both Na^+ and NH_4^+ slightly improved the RB dye adsorption capacity onto A-TRB [35].

CONCLUSIONS

+ The zeta potential of kaolinite suspensions was not dramatically changed with solid concentration.
+ The isoelecric point of kaolinite was found about pH 2.15.
+ The initial pH value of Cr(VI) solution had a strong effect on the adsorption behavior of kaolinite. The results show that chromium removal increases with decrease in pH values.
+ Adsorption removal slightly decreased with increase of the solution temperature. This shows that the adsorption process is an exothermic process.
+ Results clearly depict that the adsorbed amount of chromium (VI) was slightly higher in the presence of salt.
+ Adsorption has decreased with inreasing pH.
+ Practically good removal efficiencies of hexavalent chromium were attained in the adsorption process.
+ It is apparent that further treatment of the tannery wastewater using adsorption method by kaolinite has an effect that improving the quality of the effluent.

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PREPARATION OF MESOPOROUS CARBON WITH ENHANCED ADSORPTION PERFORMANCE ON CIPROFLOXACIN AND TETRACYCLINE

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ABSTRACT

In this work, the mesoporous carbon was synthesized through volatile organic solvents-organic self-assembly under different ratios of raw materials, using F-127 as template, phenolic resin as carbon source, tetraethyl orthosilicate (TEOS) as silicon source. Morphology and structure of prepared mesoporous carbon were characterized by X-Ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and Transmission electron microscopy (TEM). The optimized condition of ordered structure was obtained by adjusting the different ratios of raw materials. The adsorption performance was investigated by adsorption of ciprofloxacin and tetracycline. A series of adsorption were studied at different initial concentrations from 50 to 500 mg/L, and also the different temperatures from 20 to 50℃ with various mesoporous carbons which were fabricated under different ratios of raw materials. The result revealed that the best wight proportion of TEOS, phenolic resin and F127 is 3:0.667:2, and the adsorption rate of tetracycline could reach 98%. Last, the adsorption processes of tetracycline were also discussed.

KEYWORD

Mesoporous carbon materials; self-assembly; adsorption; ciprofloxacin; tetracycline

INTRODUCTION

Ciprofloxacin (CIP) and tetracycline (TC) were extensively used to treat disease, prevent and promote growth etc. [1-3]. Because of extensive use, part of antibiotics was discharged the ecological environment, which was serious harm to human，animals and plants, even bacteria itself. So, residue of antibiotics in the drinking water, even only trace levels, could affect on the body's immune system and decrease immunity. Thus, it is imperative to remove the residue of antibiotics in the water. As a result, various physical, chemical and biological methods have been designed to treat antibiotics contaminated water, such as coagulation [4], electrochemical method [5], degradation [6,7] and photodegradation [8-10] and aerobic or anaerobic treatment [11]. Among these methods, adsorption has been found to be one of the most common techniques for antibiotics removal because of its easy operation and high efficiency [12–15]. Ordered mesoporous carbon possesses big pore size, large specific area, high pore volume and chemical stability to be suitable to apply in catalysis, adsorption, electrochemistry and gas separation [16-18] . Recently, mesoporous carbon materials have been used in the adsorption process of many organic pollutants [19-23]. The results showed the adsorption was available method to remove antibiotics in the water. Various mesoporous carbon have been prepared by different routes [24-26]. Wang [25] reported that ordered mesoporous carbons with tunable pore size in the range of 3.6-6.2 nm which prepared via self-assembly method using the mixture of phenol, resorcinol and phloroglucinol as carbon precursor and triblock copolymer F127 as template. Jiang [26] reported ordered mesoporous carbons were synthesized by a simple organic-inorganic co-assembling method using sucrose as carbon precursors and n-hexane as micelle swelling agents.

In present study, ordered mesoporous carbon