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Effect of pH on the adsorption kinetics of Cr(VI) on sodium chlorite treated coconut coir

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Abstract

Coconut coir is a low cost bioadsorbent containing large amount of lignin. In this research work sodium chlorite treated coconut coir (SCT-CC) was used to remove Cr(VI) from industrial wastewater by implementing adsorption technique through the investigation of the adsorption kinetics at different pH values. The maximum Cr(VI) adsorption capacity of SCT-CC at pH 2.00, 3.00, 5.00 and 7.00 was 24.75, 23.92, 16.07 and 6.31 mg Cr(VI) g^{-1} SCT-CC respectively with the dose of 7.5 g/L. The equilibrium established within three hours resulting the maximum removal (95%) of chromium. The adsorption kinetics of Cr(VI) on SCT-CC was found to be regulated by pH of the system. Rate of adsorption was the highest at pH 2.00 and the kinetic data well-fitted with Ho's pseudo second order kinetics. Fourier transform infrared (FT-IR) spectrometry analysis indicated that the carbonyl (C=O) groups and hydroxy (O-H) groups from the lignin structure in coconut coir may be involved in the mechanism of Cr(VI) adsorption and it showed good agreement with the kinetic data to elucidate the adsorption mechanism.

Keywords: Coconut coir; Sodium chlorite; Chromium (VI); Adsorption; Kinetics; Removal

Introduction

The pollutants (inorganic or organic) induce toxic impacts on all the living entities including human being through water, soil and even air. Common diseases from the polluted water are: skin allergy and inflammations, gastroenteritis, typhoid and paratyphoid, liver diseases like hepatitis, jaundice, upper respiratory inflammations, and any of these may develop even deadlier cancers. Among the inorganic pollutants heavy metals (e.g., As, Pb, Cd, Cr etc.) are responsible for water pollution when thrown to the water without complete detoxification. Chromium exists in three common stable valence states: chromium (0), (III), and (VI). It exists in natural water in two main oxidation states, hexavalent (Cr(VI)) and trivalent (Cr(III)). The Cr(VI) has been found to be the great threat to the living organism with the advancement of the industrialization (tannery, porcelain and ceramics manufacturing, paint and pigment etc.). It can occur naturally in the earth crust, although it is primarily emitted to the environment as a result of anthropogenic activities. The occurrence and distribution of chromium in the environment have been extensively reviewed (Mukherjee, 1998; Kotas and Stasicka, 2000; Ellis *et al.,* 2002; Paustenbach *et al.,* 2003; Krystek and Ritsema, 2007).

The Cr(VI) causes serious health problem because of its uncontrolled release in the environment without appropriate treatment. It causes respiratory, skin (Bruynzeel *et al.,* 1988), carcinogenic (Dayan and Paine, 2011), renal (Kirschbaum *et al*., 1981), hepatic (Pascale *et al.,* 1952), gastrointestinal, cardiovascular (Loubieres *et al.,* 1999), hematological, genotoxic and mutagenic effects on human body.

Several studies have been carried out so far in order to find effective adsorbent to mitigate chromium from polluted water. Raji *et al.,* (1998), used batch process for removing Cr(VI) by polyacrylamide-grafted sawdust studying kinetics and thermodynamics. The process was found to be exothermic with a maximum adsorption of 91.0% at 30ºC for an initial concentration of 100 mg/L at pH 3.00. Coconut coir was also used as bioadsorbent in order to remove Cr(VI) from laboratory waste water (Gonzalez *et al.,* 2008). The research revealed that about 17% of chromium had been removed from sulphochromic waste water solution by dried coconut coir whereas 72% of chromium was removed by hydrated coconut coir. Research for investigating the biosorption of chromium from industrial waste water was also done by

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using pistachio hull waste biomass (Moussavi *et al.* 2010). Inorganic mineral as well as activated carbon are also being used for the removal of chromium from waste water. Wanees *et al.* (2012) investigated the adsorption potential of activated carbon and bentonite for the removal of Cr(VI) ions from waste water. They conducted comparative study of the adsorption of Cr(VI) on these two surfaces at different conditions, i.e., contact time, adsorbent dose, temperature, pH etc. through thermodynamic and kinetic study. Bentonite was found to be more effective adsorbent in removing Cr(VI).

In the present study raw coconut coir was modified by sodium chlorite to enhance the adsorption capacity which was not good enough in the previous study for the removal of Cr(VI) by this sort of bioadsorbent (Gonzalez *et al.,* 2008). Besides, the effect of pH on the adsorption kinetics of Cr(VI) on SCT-CC was also investigated. In this research not only the adsorption mechanism of Cr(VI) onto SCT-CC regulated by pH was revealed but the condition to increase the adsorption capacity of coconut coir by treating with sodium chlorite was also optimized.

Materials and methods

Analytical grade potassium dichromate ($K_2Cr_2O_7$) (Scharlau Chemicals, Spain) was taken as the source of Cr(VI). Coconut coir collected from the local market was utilized as adsorbent. Sodium chlorite (80% $NaClO_2$) (BDH Laboratory Supplier, England) was used for treatment of coconut coir (CC).

Single beam UV-visible Recording Spectrophotometer (OPTIZEN POP, Korea) was used to analyze Cr(VI). IR spectra of SCT-CC were recorded before and after adsorption using a FTIR spectrophotometer (Model: Frontier FT-NIR/MIR, Perkin Elmer, USA).

Fibrous coir purchased from the local market was washed with tape water for several times to remove dust and pigments and was again washed with distilled water for three times and this distilled water-washed and air-dried fiber was then kept in oven at 110ºC and the resulting crispy materials were grinded. This untreated coconut coir (UCC) was used for further treatment.

According to Box-Behnken experimental design (Liu *et al*., 2012), the previously obtained UCC was stirred with 6.2g of sodium chlorite in the presence of 9.5 mL of acetic acid for about 60 min at required rpm with designed reaction temperature 90°C. The treated coconut coir was washed with distilled water until the filtrate had reached pH 6-7, then dried at 70ºC to a constant weight, screened through sieve and put in desiccators for further use.

About 0.3g of SCT-CC (particle size of 150-300 μm) was charged in reagent bottles containing Cr(VI) solution of concentration about 200 ppm at pH 2±0.02. These bottles were shaken in the mechanical shaker at 28.0±0.5ºC. After a particular interval of time the reagent bottles were withdrawn from the shaker. The supernatant liquid was centrifuged to obtain a clear solution. The experiment was repeated at other pH values of 3.00, 5.00 and 7.00.

Chromium concentration in the solution was determined by using UV-visible spectrophotometer. The λ_{max} of the solution was found to be within 360-370 nm at all the pH values under observation.

Adsorption kinetics was investigated at four different pH values, i.e., 2.00, 3.00, 5.00 and 7.00 at the temperature of 28.0±0.5ºC.

The surface of the SCT-CC before and after adsorption of Cr(VI) at different pH values was characterized by FTIR spectroscopy in order to find out whether any shifting of IR peak due to the interaction of Cr(VI) with SCT-CC occurred or not. Based on this evidence the adsorption mechanism was hypothesized.

Results and discussion

Adsorption behaviour

The amount of Cr(VI) adsorbed (q_t) vs. time curve (Fig. 1) for the adsorption of Cr(VI) on SCT-CC was found to be similar with the usual curves. Two major observations may be noted. In one case, the initial sharp increase of the amount of Cr(VI) adsorbed onto SCT-CC and the attainment of the steady value were eventually observed.

Comparatively gradual increase of the curve followed by the slow attainment of the steady value was observed in the other case.
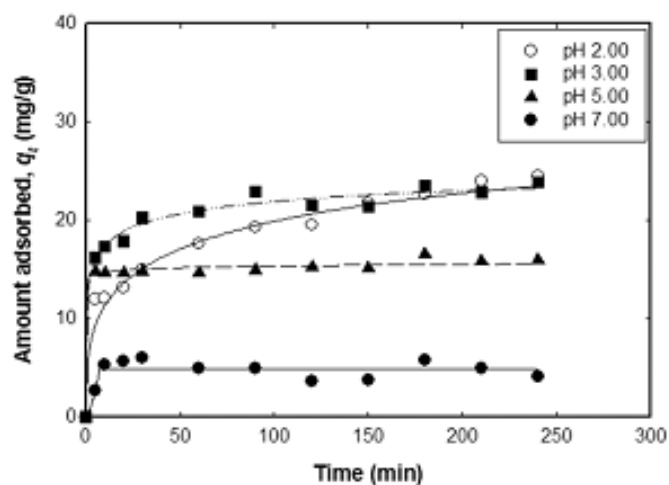
Fig. 1. Variation of amount of Cr(VI) adsorbed (q_t) on SCT-CC at different pH values at 28.0±0.5 °C.

Fig. 2. Variation of concentration of Cr(VI) during the adsorption on SCT-CC at different pH

Effect of pH on equilibrium time

The equilibrium time for the adsorption of Cr(VI) onto SCT-CC was found to be influenced by the pH of the system (Fig. 1). After the quick increase of the amount adsorbed at the beginning, the adsorption of Cr(VI) on SCT-CC reached the equilibrium within 50 min at higher pH values (i.e., pH 5.00 and 7.00). However, at lower pH values (such as pH 2.00 and 3.00) the system was found to take about three h to attain the equilibrium. The amount of Cr(VI) adsorbed on SCT-CC was observed to be the highest (24.75 mg/g) at pH 2.00 and the lowest (6.31 mg/g) at pH 7.00. The percent removal of Cr(VI) from aqueous solution was found to be around 95% at lower pH by using SCT-CC. Chromium in potassium dichromate solution exists as composite anion ($Cr_2O_7^{2-}$). When the pH was raised to 7.00 the surface of SCT-CC became negative and the repulsive force acted between adsorbate and the surface. As the pH of the medium was decreased to 2.00 the surface became positive. The negatively charged dichromate was adsorbed on the surface predominantly due to the electrostatic force of attraction.

Adsorption kinetics

The kinetics of the adsorption of Cr(VI) on SCT-CC was found to be regulated by controlling the pH of the system. The adsorption process slowed down as the pH of the solution was increased (Fig. 2). It was manifested by calculating the rate of adsorption which dropped as the pH of the solu
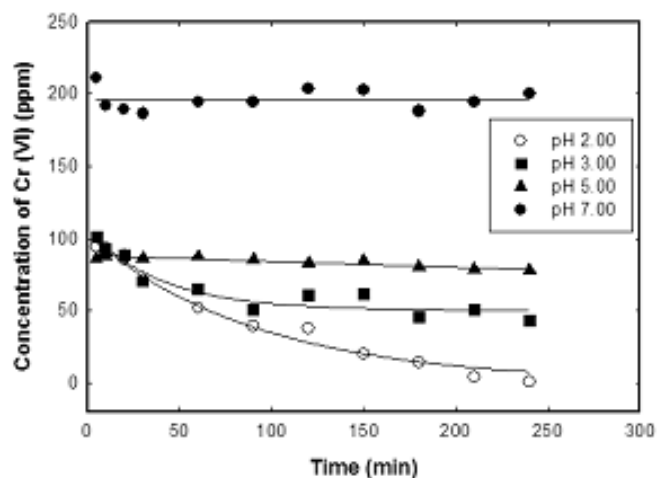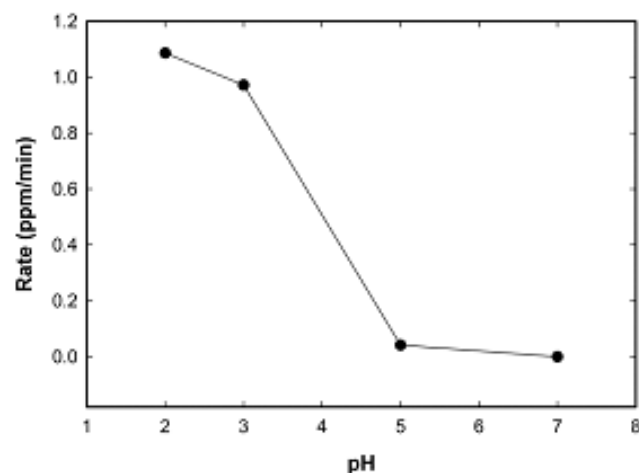

Fig. 3. Variation of rate of adsorption of Cr(VI) on SCT-CC with pH at 28.0±0.5 °C.

tion was increased (Fig. 3). The data for the adsorption of Cr(VI) on SCT-CC at different pH values were investigated whether they follow the Lagregran pseudo-first-order or Ho's pseudo second order kinetics (Ho *et al.,* 1996). The data obtained from the determination of equilibrium time for the adsorption of Cr(VI) on SCT-CC were fitted in Ho's pseudo second order kinetic equation (Fig. 4). The value of correlation coefficient, R^2, was found to be within 0.941-0.998 depending on different pH values (Table I).

However, data at acidic pH values were found to be better fitted with the kinetic model mentioned above than the neutral one.

Table I.Kinetic data for the adsorption of Cr(VI) on SCT-CC

pH	Second-order kinetic model		
	q_e (mg/g)	k_2 (g mg^{-1} min^{-1})	R^2
2.0	23.34	2.43 x 10^{-3}	0.987
3.0	23.1	7.34 x10^{-3}	0.996
5.0	15.6	20.87 x10^{-3}	0.998
7.0	4.88	123.03 x10^{-3}	0.941
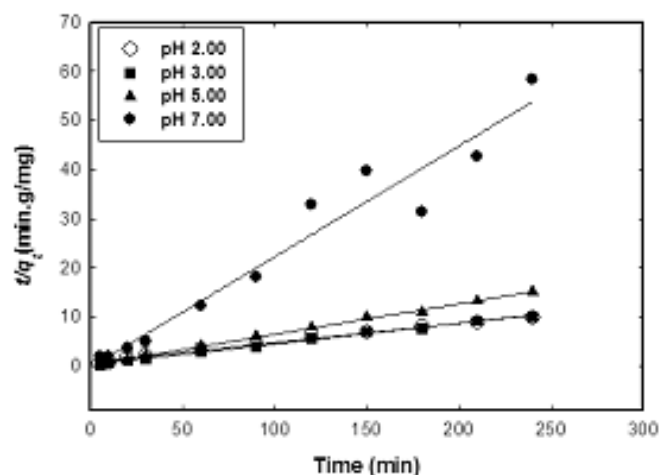
Fig. 4. t/q_t **vs. time for fitting with Ho's equation of pseudo second order kinetics at different pH values**
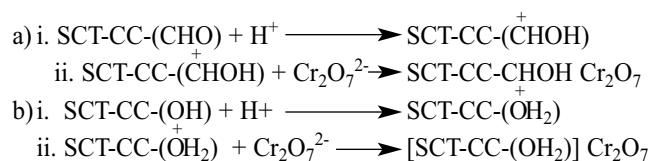
FTIR spectra analysis and adsorption mechanism

FTIR spectra are commonly used to identify the groups involved in the reaction process and thus the FTIR spectra of bare SCT-CC and Cr(VI) adsorbed SCT-CC at different pH values were investigated and are shown in Figure 5. The band for the stretching vibration of -OH in cellulose of coconut coir was found to become broader at 3429.0 cm^{-1} in the case of bare SCT-CC, which might be due to the formation of hydrogen bond after treatment. This broader band became comparatively sharper and shifted to the higher frequency (3440.7 cm^{-1}) after the adsorption of Cr(VI) when the pH of the solution was decreased up to 2.00. This may occur due to the destruction of hydrogen bond due to the protonation of the surface. However, at higher pH (7.00) FTIR spectrum of the adsorbed surface was found to be similar to the bare surface. This indicates the very weak interaction between Cr$_2$O$_7^{2-}$ and SCT-CC occurring at neutral pH. A feeble shoulder at 2854.8 cm^{-1} was found in the case of bare surface which depicted the presence of aldehydic -CHO. The
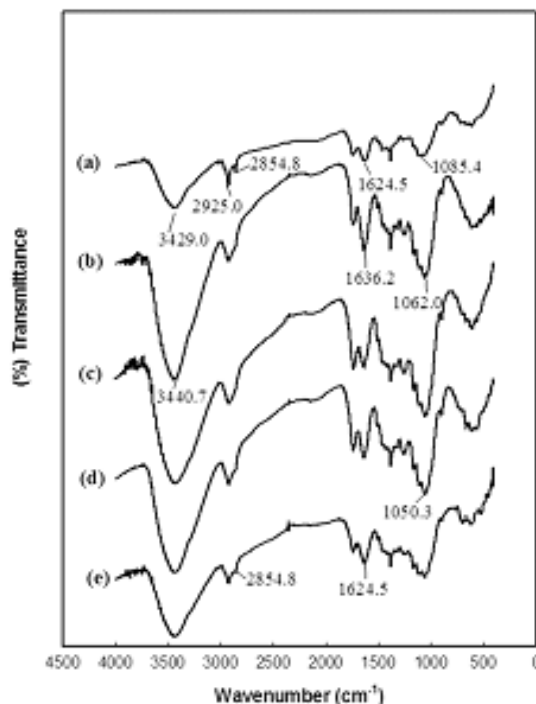
Fig. 5.   FTIR spectra of (a) bare SCT-CC, (b) Cr(VI) adsorbed SCT-CC at pH 2.00, (c) pH 3.00, (d) pH 5.00 and (e) pH 7.00

band at 2854.8 cm^{-1} diminished at pH 2.00 to 5.00. This might be due to interaction of Cr$_2$O$_7^{2-}$ with the available carbonyl carbon of lignin in SCT-CC. The weak single (2854.8 cm^{-1}) reappeared when the pH was increased to 7.00.

Another band at 1624.5 cm^{-1} indicated the existence of C=C in bare SCT-CC. This band became more intense and shifted to little higher frequency (1636.2 cm^{-1}) in the case of lower pH. However, at higher or at neutral pH the intensity becomes lower due to very weak interaction of the Cr(VI) with the surface.

Proposed mechanisms

a) i. SCT-CC-(CHO) + H$^+$ $\longrightarrow$ SCT-CC-(C̊HOH)
   ii. SCT-CC-(C̊HOH) + Cr$_2$O$_7^{2-}$ $\longrightarrow$ SCT-CC-CHOH Cr$_2$O$_7$
b) i. SCT-CC-(OH) + H+ $\longrightarrow$ SCT-CC-(O̊H$_2$)
   ii. SCT-CC-(O̊H$_2$) + Cr$_2$O$_7^{2-}$ $\longrightarrow$ [SCT-CC-(OH$_2$)] Cr$_2$O$_7$

The above mechanism was proposed based on the evidence obtained from the FTIR data. The gradual sharpness of the peak for O-H group as well as the disappearance of the peak for C=O (aldehydic) as the pH was decreased indicated the

interaction between the protonated surface with the negatively charged $Cr_2O_7^{2-}$ present in the solution. The interaction of $Cr_2O_7^{2-}$ with the protonated SCT-CC seemed to follow the nucleophilic addition as is usually observed in some organic compounds under acidic condition. The negatively charged $Cr_2O_7^{2-}$ underwent the nucleophilic addition with SCT-CC at lower pH through the electrostatic force of attraction.

Conclusion

The quick attainment of the equilibrium for the adsorption of Cr(VI) onto SCT-CCT was found to occur at pH 5.00 and 7.00. The lower value of pH (2.00 and 3.00) was observed to facilitate the adsorption mechanism and it took longer time to reach the equilibrium with the outcome of large amount of chromium adsorbed on SCT-CC. The adsorption kinetics was found to be influenced by the action of the pH of the solution. The high value of the rate of adsorption was observed at pH 2.00 and 3.00. However, this rate was found to fall drastically when the pH was increased to 5.00 and 7.00. The kinetic data indicated that the interaction between the Cr(VI) ($Cr_2O_7^{2-}$) and SCT-CC is fully electrostatic. Because of the electrostatic force of attraction between negatively charged adsorbate species and positively charged adsorbent reinforced the rate of adsorption at lower pH whereas the neutral pH showed very much weaker interaction between adsorbate and adsorbent.

Acknowledgement

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