Adsorption of Cr (VI) onto Wollastonite: Effect of pH

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Wollastonite, a clay mineral has been investigated for the adsorption of Cr(VI). Adsorption of chromium was studied as a function of pH and 2.0, 5.0, 6.0, and 8.0 pH were selected for studies. Maximum adsorption was found (74.4%) at pH 2.0, temperature 30°C, 0.5x10^{-4} M Cr(VI) concentration, 0.01 M NaClO₄ ionic strength and 100 rpm of agitation speed. It was, however, minimum (12.3%) at pH 8.0. Equilibrium time of adsorption was independent of pH values. Different possible explanations have been discussed for removal of Cr(VI) for the present system. Kinetics of the removal of Cr(VI) at various pH values has been discussed and rate constant of the adsorption has been determined.

Chromium is an important metal having a variety of applications. It is extensively used in electroplating, leather tanning, paints and pigments and other allied industries. Chromium enters water resources through discharge of untreated industrial effluents. Chromium is a toxic metal and its adverse effects on fauna, flora and human beings are well documented. It has been reported to be a potent carcinogen producing cancer of various parts of the body. Because of the toxic nature of Cr(VI) this metal is of concern to scientific workers. Various technologies available for the treatment of Cr(VI) rich wastewaters include ion-exchange, solvent extraction, chemical precipitation etc. But these methods are cost intensive and are unaffordable for large scale treatment of wastewater rich in Cr(VI) for developing nations like India. Adsorption on activated carbon is also an expensive method for the treatment of industrial effluents and is quite popular in developed countries. In order to reduce the cost of activated carbon treatment cheap and waste materials have been tried for reclamation of wastewater from various industries. In the present work wollastonite, a clay mineral, found in plenty in India has been used as adsorbent for removal of Cr(VI) from aqueous solutions and wastewaters. The present communication has been addressed to the effect of pH on the removal Cr(VI) from water and wastewater.

Experimental Procedure
All the chemicals used in the experiments were of AR/GR grade and were supplied by B.D.H., Bombay, India. The wollastonite was taken from the foundry workshop of the Institute. It was graded as desired and used as such in the experiments without any treatment to avoid extra expenditure. The average particle size of the adsorbent was maintained at 100 μM. The average particle size of the adsorbent was measured by Langmuir's adsorption method using an HIAC – 320, model 800 2917 (Rayco Instruments Div., USA) and surface charge by using a lazer zee Meter, Model 500 (Penkem Inc., N.Y.). The surface area was determined by a triple point N₂ gas adsorption method employing a Quantasorb Surface Area Analyser, Model QS – 7 (Quantachrome Crop., N.Y.) and porosity by the mercury intrusion method using a mercury porosimeter carloebra Model 2000 (N.Y., USA). Standard method was used to analyse the adsorbent chemically.

Batch adsorption experiments were carried out by shaking 20 g/L of the adsorbent with 50 mL of Cr(VI) solutions of desired concentrations. Initially solutions containing concentrations viz 0.5x10^{-4}, 1.0x10^{-4}, 1.5x10^{-4} and 2.0x10^{-4} M of Cr(VI) were taken in different glass bottles at 100 rpm, 0.01 M NaClO₄ and 30°C temperature. At the predetermined time intervals, the adsorbent was removed from the solutions by centrifugation and the progress of adsorption was determined spectrophotometrically using a spectrophotometer, model UV – 2100, Shimadzu, Japan. pH of the samples was maintained by adding 1.0 M NaOH/HCl solutions.
Results and Discussion

Characterization of the adsorbent

The physical and chemical analysis of the adsorbent was carried out and the results are presented in Table 1. Table 1 shows that CaO and SiO$_2$ are the main constituents of wollastonite and oxides of other metallic species are present as traces in it. This indicates that these two components would be responsible for the adsorption of Cr(VI) from the bulk solution onto wollastonite. The value of porosity reveals that the adsorbent is adequately porous in nature.

Effect of contact time and pH

The study of effect of pH on the adsorption of Cr(VI) on wollastonite is useful in two ways viz. fixation of the optimum pH for the removal of Cr(VI) from the aqueous solution onto surface of the adsorbent and also regulating the chemical species of Cr(VI) in the solution. At pH <1 the dominant species is H$_2$CrO$_4$ whereas between 2 – 6 pH there is an equilibrium between HCrO$_4$$_{-}$ and Cr$_2$O$_7^{2-}$. Beyond pH 6.0 the major component is CrO$_2^{2-}$. The specification of chromium species has been given in Fig. 1. The results on the adsorption of Cr(VI) at different pH show that for all the values of pH the adsorption increased gradually till it acquired equilibrium in 100 min. The maximum removal (74.4%) (Table 2, Fig. 2) was observed at pH 2.0 at 0.5×10$^{-4}$ M Cr(VI) concentration, 0.01 M NaClO$_4$ ionic strength, 100 rpm and 30°C temperature. The maximum removal at pH 5.0, 6.0 and 8.0 was found to be 53.8, 37.8 and 12.3% respectively (Table 2, Fig. 2).

Out of the several studies made for removal of Cr(VI) by adsorption on powdered activated carbon
Cr(VI) at neutral and negatively charged surface can not be explained on the basis of electrostatic attraction only. Specific chemical interactions and surface complexation have been suggested to operate during the adsorption of Cr(VI) on wollastonite. It seems that the adsorption beyond pH 4.5 will include CrO$_2^{2-}$ ions (Fig. 1) and the following surface complexation scheme has been suggested$^{16}$ for the uptake of Cr(VI):

$$\text{(SOH)}_2 + 2\text{H}^+ + \text{CrO}_4^{2-} \leftrightarrow \text{CrO}_4^{2-} \quad \ldots (1)$$

An alternative scheme based on chemisorption includes HCrO$_4^{-}$ and CrO$_4^{2-}$ for Cr(VI) removal$^{17-19}$. The maximum adsorption of Cr(VI) around pH 2.0 may be associated with dissociation of the substrate and release of Ca$^{2+}$ from wollastonite and its interaction with the dominating HCrO$_4^{-}$ species leading to formation of surface compounds$^{20-22}$:

$$\text{M}^{2+} + \text{HCrO}_4^{-} \leftrightarrow (\text{M}^{1+}\text{HCrO}_4) \quad \ldots (2)$$

where M stands for Ca$^{2+}$ or any other metallic species.

It is argued that at pH $\equiv$ 2.0 a significantly high electrostatic attraction exists between adsorbent and adsorbate and this results in the formation of surface compound$^{23,24}$. In the acidic range there is presence of Cl$^{-}$ in the double layer and chromate – chloride ion exchange has also been suggested$^{25}$ to explain the Cr(VI) removal by wollastonite:

$$2\text{RCI} + \text{CrO}_4^{2-} \leftrightarrow \text{R}_2\text{CrO}_4 + 2\text{Cl}^- \quad \ldots (3)$$

(PAC) or granular activated carbon (GAC)$^{12-15}$ some are oriented towards treatment of industrial wastewaters. In a study 10.0 g/L batchwise quantity of GAC was used for Cr(VI) removal over the pH range of 2 to 10$^{14}$. The maximum removal occurred at pH 2.0, whereas, there was an exponential decrease of effectiveness to a pH value of about 6.0. In another batch study$^{15}$, 10,000 mg/L quantity of Filtrasorb 400 activated carbon was used for Cr(VI) and Cr(III) removal. The GAC responded in somewhat different manner to pH variations. Virtually no adsorption occurred below pH 2.0 or above pH 8.0, with the maximum occurring at pH values 5 to 6.

The variation in adsorption of Cr(VI) on wollastonite has further been given in Fig. 3. The pH$_{pzc}$ of wollastonite viz. 2.6 (Table 1) indicates that the surface is positively charged at pH $\equiv$ 2.0 and will be quite favourable for adsorption of the dominating HCrO$_4^{-}$ species at this pH. Significant adsorption of

![Fig. 3—Time variation for the adsorption of Cr(VI) on wollastonite at different pH values](image-url)
The pH dominated adsorption, however, does not support the above view in the present case for a wider range of pH.

**Kinetic Modelling**

The complete understanding of effect of pH on adsorption of Cr(VI) from bulk onto surface of wollastonite requires knowledge of its kinetics. For the present investigations, the kinetic modelling was carried out using Lagergren’s model 21:

\[
\log(q_e - q) = \log q_e - \frac{2.303}{K_{ad} t} \quad \text{... (4)}
\]

where \(q_e\) and \(q\) (both mg g\(^{-1}\)) are the amounts of Cr(VI) adsorbed at equilibrium and at time \(t\), respectively, \(K_{ad}\) (min\(^{-1}\)) is the rate constant of transfer of Cr(VI) onto wollastonite surface. The plots between \(\log (q_e - q)\) versus \(t\) (Fig. 4) are linear and this shows that the present system follows a first order kinetics. The values of \(K_{ad}\) for Cr(VI) uptake at pH 2.0, 5.0, 6.0 and 8.0 were determined and are given in Table 2. This is clear from this Table that with increasing pH, the rate constant reflected a decreasing trend. The value of \(K_{ad}\), at pH 2.0, 30°C temperature, \(5.0 \times 10^{-4}\) M Cr(VI)
Effluents from aqueous solutions and industrial complexes seem to operate during adsorption of Cr(VI) on wollastonite.

Conclusions

Based on the above experiments the following conclusions may be drawn:

(i) pH is an important parameter in removal of Cr(VI) from aqueous solutions and industrial effluents.

(ii) Specific chemical interactions and surface complexation seem to operate during adsorption of Cr(VI) on wollastonite.

(iii) Equilibrium time is independent of pH.

(iv) Maximum removal was obtained at pH 2.0 under optimum conditions.

(v) Studies may be extrapolated for treatment of wastewater rich in Cr(VI).

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Table 3—Values of rate constant of adsorption of Cr(VI) on wollastonite at different pH

<table>
<thead>
<tr>
<th>pH</th>
<th>$K_a$ (min$^{-1}$)</th>
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<tbody>
<tr>
<td>2.0</td>
<td>4.61 $\times 10^{-2}$</td>
</tr>
<tr>
<td>5.0</td>
<td>3.26 $\times 10^{-2}$</td>
</tr>
<tr>
<td>6.0</td>
<td>2.30 $\times 10^{-2}$</td>
</tr>
<tr>
<td>8.0</td>
<td>1.28 $\times 10^{-2}$</td>
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Concentration, 100 rpm, 0.01 M NaClO$_4$ ionic strength was found to be $4.61 \times 10^{-2}$ min$^{-1}$ (Table 3).

Cost analysis

Wollastonite, the clay mineral used as adsorbent in the studies is available in plenty in India with its reserves at Udaipur (Rajasthan) and it has been used in the experiments without any chemical treatment after crushing. Though a detailed cost analysis of the process has not been carried out, it is clear that no extra cost is incurred in application of wollastonite for water and wastewater treatment and it can be an ideal alternate to the expensive activated carbon.

References

3. Mukerjee AG (Ed) Environmental Pollution and Health Hazards: Causes and Control (Galgotia, N.D.), 1986.