



Removal of Cr (VI) from Gomati river by wollastonite

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Abstract

Chromium exists in two forms mainly Cr(III) and Cr(VI) and out of them Cr(VI) is highly toxic and is documented as high priority pollutant. It has attracted the attention of the scientist workers worldwide. The present work was addressed to the use of clay mineral, wollastonite in order to provide an economically viable treatment of Cr(VI) containing aqueous solutions and industrial effluents present in Gomati River. The removal of chromium is found to be concentration dependent. In case of Cr(VI) removal effect of adsorbent dosages maximum removal was found 3.0 g/L i.e. 98.88% at initial concentration of 100 g/L. Maximum removal of Cr(VI) observed in 90 min to 120 min in all concentration of solutions because number of reactive surface area of wollastonite is more. At 90 to 100°C of reaction temp., adsorption capacity of wollastonite increase due to chemical interaction between adsorbed and adsorbent. Maximum removal of Cr(VI) occurs at pH 2.0 (98.42%) in 100 mg/L initial concentration of solution. The maximum removal of Cr(VI) was 92.76% at 100 mg/L solution concentration. After 100 rpm agitation removal of Cr(VI) approximately achieved equilibrium. Smallest particle size of wollastonite 0.225mm have greater adsorption capacity of Cr(VI).

Key words : Cr (VI), Removal, Kinetics, Intraparticle diffusion, Thermodynamic parameters.

Introduction

Chromium is distributed on the earth's crust at approximately 100 ppm levels. It exists in many valence states like metallic chromium, bivalent chromium, trivalent and hexavalent chromium but from environmental viewpoint, two of its forms, viz., trivalent Cr(III) and hexavalent Cr(VI) are important¹. Its hexavalent form is well known highly toxic metal and is considered to be a priority pollutant².

After flowing southwards of Gomati river through the districts of Sitapur, Lucknow, Barabanki, Sultanpur and Jaunpur it confluences with River Ganga in Kaithi, Ghazipur bordering Varanasi. For about 450 km from the origin, the difference in the elevation is about 100m amsl. For the remaining stretch of 500 km, there is an elevation difference of 25m.

On the banks of the river, Sitapur, Lucknow, Sultanpur and Jaunpur are the four major urban settlements. The river, subsequently receives the untreated wastewater and effluents from these locations in its course through more than 45 major drains. Throughout its stretch, there are many tributaries such as- Kathina, Bhainsi, Sarayan, Gon, Reth, Sai, Pili and Kalyani, originating within short distances and carrying the wastewater and industrial effluents from different towns and industrial units in the basin. Besides Lucknow, it supplies drinking water to other towns located on its banks. These include Lakhimpur Kheri, Sultanpur and Jaunpur. While each of these towns pollutes the river, the condition is the worst in Lucknow where most of the stretches of the river look like a drain³.

An important work on field observation of chromium on tannery sludge has been studied⁴. The present work addresses to the reclamation of Cr(VI) containing water and wastewaters by economically viable material, wollastonite, to make the process of treatment cost effective. The effect of various important parameters, viz., contact time and initial concentration, pH and temperature on the removal has been investigated. Kinetic modeling of the process of removal and possibility of intraparticle diffusion have been proposed for further study.

Wollastonite a naturally occurring, easily available, acicular, inert, white mineral

(calcium metal silicate) of high elastic modulus and its fibres are less expensive than steel or carbon micro-fibres. Wollastonite micro-fibres (WMFs; length, 0.4-0.6 mm; diam, 25-150 μ m) are very fine fibres (aspect ratio 3: 1-20:1) and used in many synthetic and ceramic products as a micro-fibre reinforcement. This paper deals with an attempt to utilize wollastonite as an adsorbent for removal of chromium and to replace costly adsorbent such as activated carbon etc.

Experimental

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 Varanasi. It was graded as desired and used as such in the experiments without any treatment to avoid extra expenditure. The surface area was determined by a triple point N₂ gas adsorption method employing a Quantasorb Surface Area Analyser, Model QS - 7 (Quantachrome Corp., N.Y.) and porosity by the mercury intrusion method using a mercury porosimeter Carloerba Model 2000 (N.Y., USA). Standard method was used to analyse the adsorbent chemically⁵.

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. 0.5×10^{-4} , 1.0×10^{-4} , 1.5×10^{-4} and 2.0×10^{-4} M of Cr(VI) were taken in different glass bottles at 100 rpm, 0.01M 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.

Batch adsorption studies

The batch tests were carried out in glass-stoppered, Erlenmeyer flasks with 200 ml working volume, with a concentration of 10 mg/L. A weighed amount (0.75 g) of adsorbent was added to the solution. The flasks were agitated at a constant speed of 500 rpm for 90 minutes in an arbitrary shaker at 303K. The influence of pH (2.0-8.0), initial Cr(VI) concentration (10, 20, 30, 40, 50, 60, 70, 90, 100 mg/L), contact time (15, 30, 45, 60, 75, 90, 105, 120, 135, 150 min), adsorbent dosage (0.25, 0.5, 0.75, 1, 1.5, 2, 2.5, 3g) and agitation speed (100, 200, 300, 400, 500,

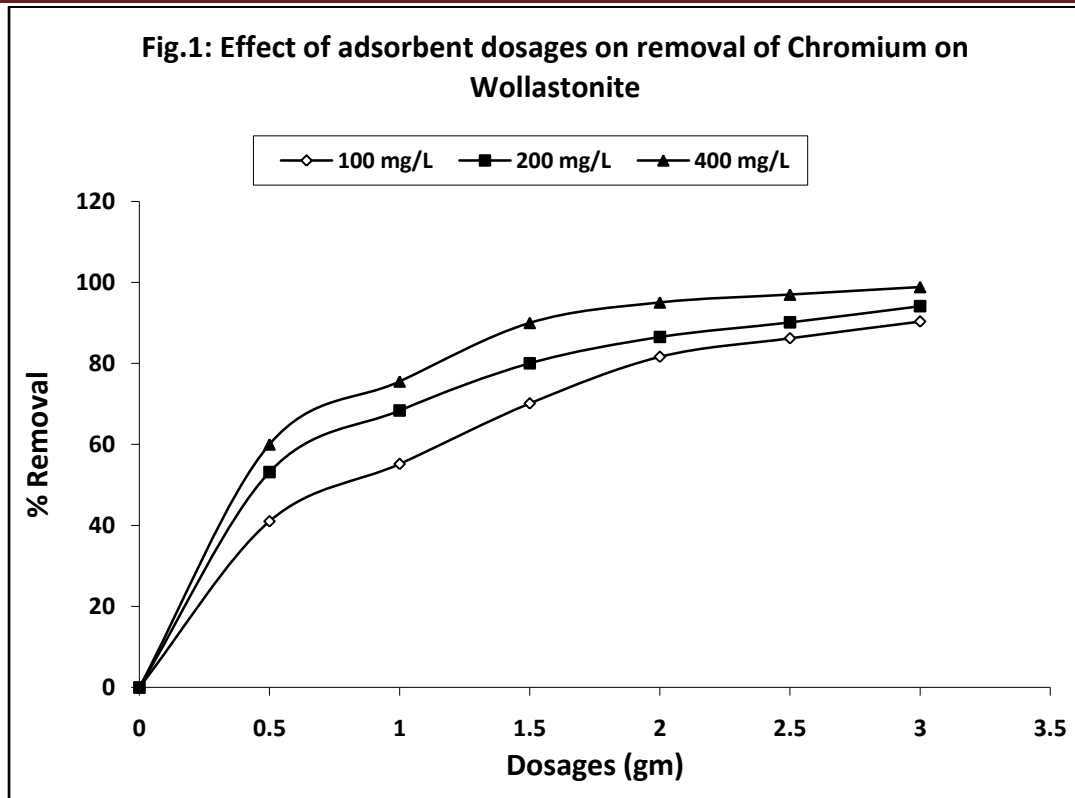
600, 700, 800 rpm) were evaluated during the present study. Samples were collected from the flasks at predetermined time intervals for analyzing the residual chromium concentration in the solution. After attaining the equilibrium, adsorbent was separated by filtration using Whatman filter paper and the aqueous – phase concentration of metal was determined by UV-V is spectrophotometer. The concentration of chromium left in the solution was determined by the standard spectrophotometric method using diphenylcarbazide as the complexant for chromium⁶. Diphenylcarbazide react with Cr(VI) in acidic medium to give a red-violet complex at 540nm. The color intensity is proportional to the concentration of Cr(VI) in the solution. The Cr(VI) concentration in solution was determined by the colorimetric method by using the obtained standard fitting equation⁷. The percentage of removal of chromium ions was calculated from the following equation:

$$\% \text{ Adsorption} = \frac{C_o - C_e}{C_o} \times 100$$

Result & Discussion

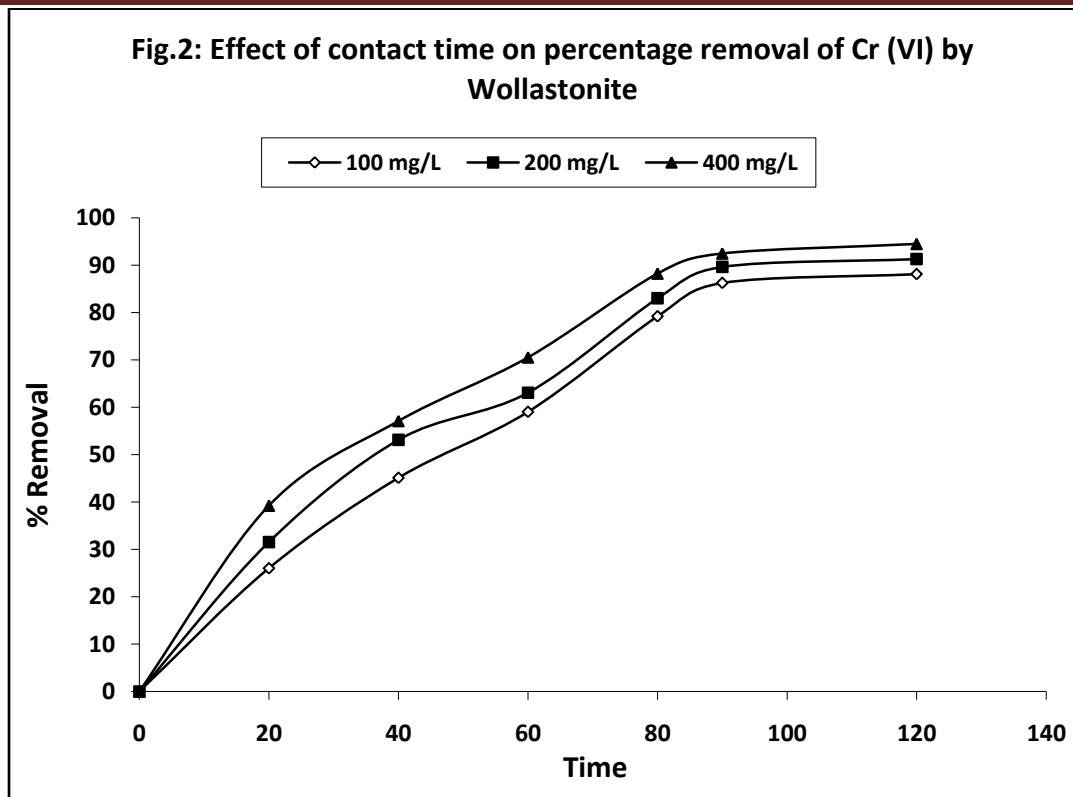
Effect of adsorbent dosages on removal of Cr (VI)

The amount of Wollastonite affects the removal percentage of Cr (VI) on aqueous solution to a large extent. When increases adsorbent dosage from 0.5 to 3.0 gm/L, the removal of Cr (VI) increase 41.02% to 98.88%. When we take solution initial concentration of 400 mg/L the removal percentage of Cr (VI) increase 41.02%, 55.18%, 70.13%, 81.64%, 86.21% and 90.35% on adsorbent dosages at 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 gm/L respectively. The minimum and maximum Chromium removal percentage was found 53.18% to 96.19% at initial concentration 200 mg/L and 60.01% to 98.88% at 100 mg/L initial concentration of solution on same dosages of Wollastonite. The behavior of above observation shows that availability of maximum adsorbent provides more adsorption site for removal of Chromium ion⁸. The increase in adsorption removal of Cr (VI) may be due to the fact that some adsorption sites may be unsaturated during the adsorption process. Number of reactive site utilize for adsorption increase by increasing the adsorbent dosages which result in the increase of removal capacity.



Effect of contact time on removal of Cr (VI)

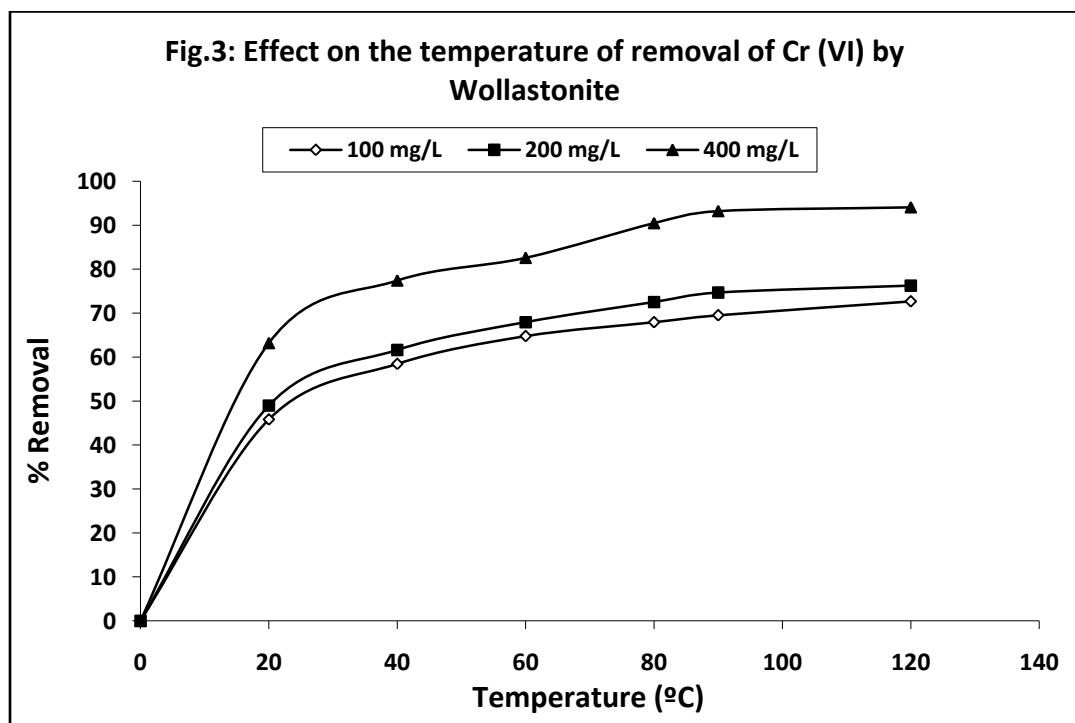
The amount of Cr (VI) adsorbed on Wollastonite at different time for different initial concentration of Chromium presented in fig.-2. The removal of Chromium rapidly increased from 20 min to 90 min. The maximum and minimum removal of Chromium from 400 mg/L initial concentration was found 26.02% to 86.25%. Removal of chromium from 200 mg/L initial concentration was found 31.54%, 53.12%, 63.08%, 83.01%, 89.64% and 91.30% in 20, 40, 60, 80, 90 and 120 min respectively. When initial concentration of chromium raise 400 mg/L the minimum and maximum removal of chromium was found 39.23% to 94.48%. Experimental pH 2.0 kept constant which ensures all Cr (VI) species in solution were negatively charged⁹.



Removal of Cr (VI) dependent on contact time with adsorbate and adsorbent amount of Cr (VI) adsorbed increased sharply upto 90 minutes in all concentrations of chromium. It was found that complete removal of chromium takes place only 100 mg/L initial concentration of chromium after 90-120 min contact time. At low initial Cr (VI) concentration, the number of reactive surface area of Wollastonite is more, therefore increasing the possibility of interaction between positively charged groups on Wollastonite with Cr (VI). However the numbers of active sites are lower when initial chromium concentration increases. It concludes that increasing Cr (VI) concentration; create competition amongst its species for positively charged groups on surface area of Wollastonite in different duration of times which result in reduction of Cr (VI) removal by Wollastonite. The percentage of chromium removal is higher in the beginning which might to due to availability of more surface area of Wollastonite. With time, the surface sites become exhausted and equilibrium achieved. At this point, adsorption rate can be regarded to be controlled by the rate at which Cr (VI) transported from solution to adsorbent particle¹⁰.

Effect of the temperature on removal of Cr (VI)

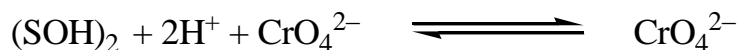
The mode of adsorption process occurring on wollastonite is exothermic in nature. In all the cases temperature has tremendous effect on the process of adsorption. Experimental result for the adsorption of chromium on Wollastonite is endothermic. At different temperature adsorption of chromium on different time interval presented figure-3. The removal of Cr (VI) increased from 45.82% to 94.08% on increasing temperature from 30°C to 50°C. In this case solution concentration was kept 100 mg/L, pH 2.5 which produce ionic strength of 0.01 M NaClO₄. The increasing pattern of removal at high temperature indicates endothermic nature of Cr (VI) removal¹¹.



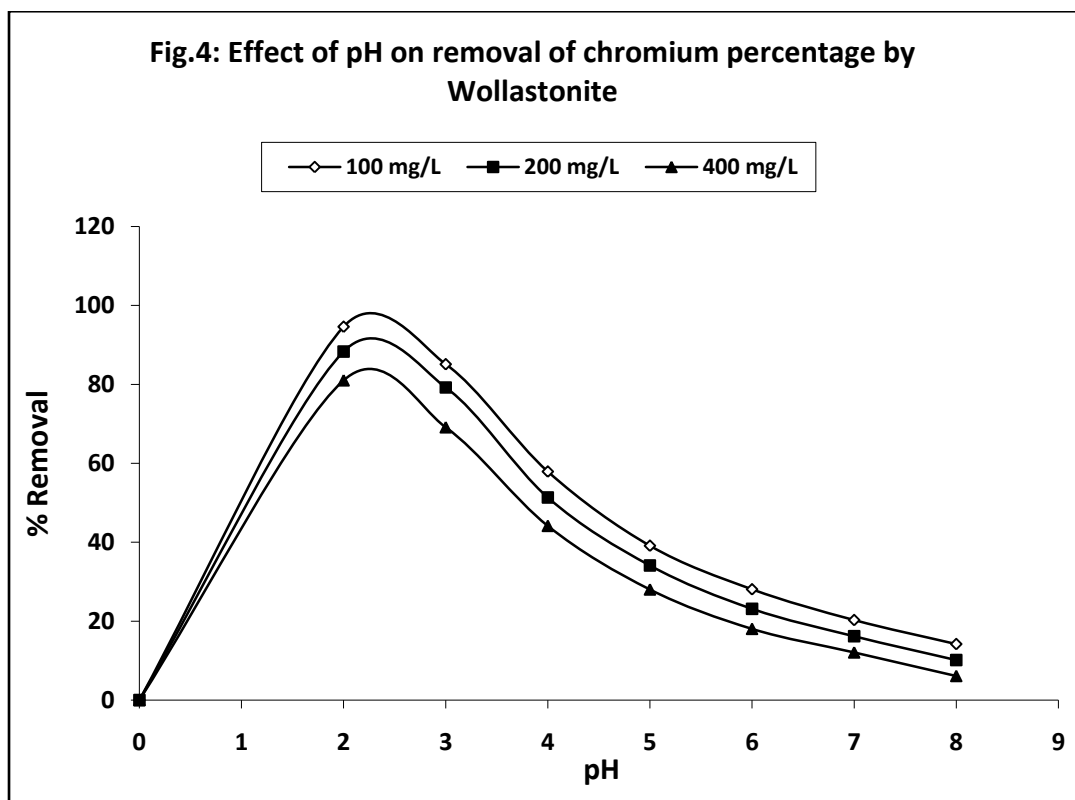
When alkali solution process at 30°C of Wollastonite minimum and maximum removal of Cr (VI) was 45.82% to 72.68% at 40°C, 48.98% to 74.26% and at 50°C 63.20% to 94.80%. The enhancement in the adsorption capacity of Wollastonite might be due to the chemical interaction between adsorbed and adsorbent. It creates some new adsorption sites by increasing the rate of intra-particle diffusion of Cr (VI) ion into the pores of the Wollastonite at higher temperature¹².

Effect of pH on removal of Cr (VI)

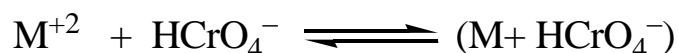
pH is an important parameter which termed as ‘master variable’ in adsorption process. The removal percentage of Cr (VI) decreases with increasing pH of solution from 2.0 to 8.0 at initial chromium concentration to 100, 200, 400 mg/L at 30°C. Wollastonite is rich in various oxides (SiO₂, CaO₂, Al₂O₃, Fe₂O₃). These undergo surface hydroxytation forming hydroxyl compound.



An alternative scheme based on process of chemisorptions which comprises HCrO₄⁻ and CrO₄²⁻ for chromium removal from solution. The maximum adsorption of Cr (VI) takes place approximately pH-2 which may be due to association and dissociation of substrate and removal of Ca⁺⁺ from Wollastonite particle. In this case HCrO₄⁻ accelerates formation of surface compounds. The effect of pH on removal of Cr (VI) presented in Fig.-4.

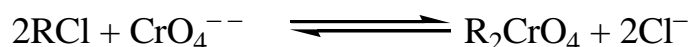


The interaction between Wollastonite with the dominating HCrO_4^- species leading to formation of surface compounds¹³. It was found that maximum removal of Cr (VI) occurs at pH 2.0 i.e. 94.82% in 100 mg/L initial concentration of solution. Removal of Cr (VI) was 88.29% in from 200 mg/L solution and 81.01% on 400 mg/L initial chromium concentration solution. In alkali range at pH 8.0 it was decreased 14.56%, 10.13% and 0.610% respectively.



Where M stands for Ca^{++} of Wollastonite

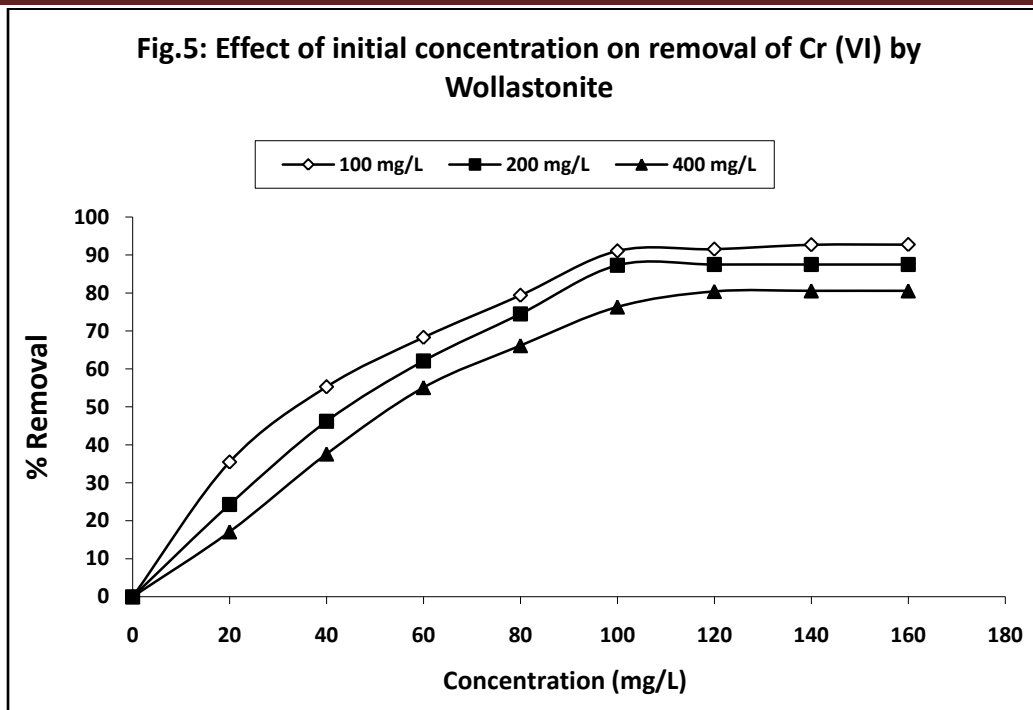
At pH 2.0 there was significantly exist higher electrostatic attraction exists between adsorbent and adsorbate. Due to this attraction formation of surface compound takes place¹³. In the acidic pH range there is presence of Cl^- in double layer and chromate-chloride ion exchange takes place. To explain the Cr (VI) removal by Wollastonite.



Higher pH of solution however does not support the above view in the present case for a wider range of pH¹⁴.

Effect of initial concentration on removal of Cr (VI)

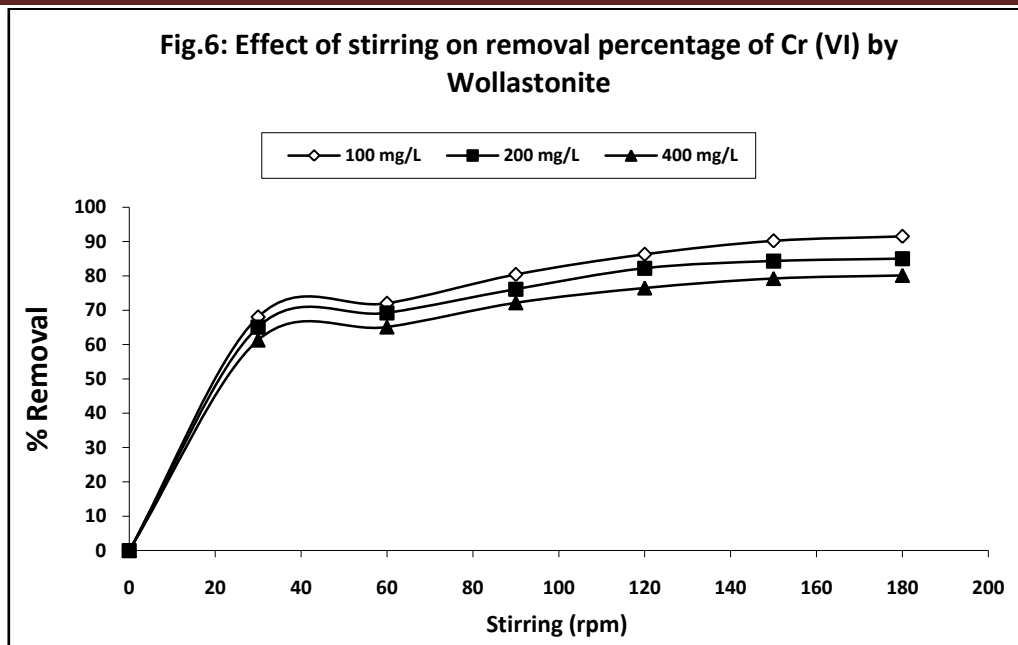
The effect of various initial concentration of Chromium adsorbed on Wollastonite shown in Fig.-5. The adsorption rate as rapid in early stage but gradually decreases in 100 mg/L, 200 mg/L and 400 mg/L concentration of Chromium adsorbed on 3.0g of Wollastonite at different pH for 90 minutes keeping constant at 30°C temperature. Increasing initial concentration of chromium decrease removal percentage of chromium at from 100 mg/L to 400 mg/L. The minimum and maximum removal percentage of Chromium at 100 mg/L was 35.49% to 92.76% at 200 mg/L was 24.30% to 87.50% and 400 mg/L was 17.10% to 80.56%. It shows that Cr (VI) removal was dependent on the initial concentration of Chromium but amount adsorbed increased with increasing initial Cr (VI) concentration. Complete chromium removal was only removed at 50 mg/L and 100 mg/L concentration after 90 and 105 minutes. The possible explanations may be availability of adsorption site on Wollastonite¹⁵.



Higher chromium concentration of solution Cr (III) ion will be release into the aqueous phase which may be due to electronic repulsion between positively charged group. Cr (III) ion had are complex of Cr (III) ion capable to bind Cr–O bond¹⁶. At low chromium concentration the ratio of active surface site is available more from adsorbent hence all metal ions interact with adsorbent and are removed quickly from the solution. However the amount of metal ions adsorbed on active sites of adsorbent is higher at high concentration¹⁷.

Effect of stirring on removal percentage of Cr (VI)

Hexavalent Chromium has low electron density which interferes in solution at variable initial concentration of Chromium solution i.e. 100 mg/L, 200 mg/L and 400 mg/L. On different mixing speed removal percentage of Cr (VI) are presented in Fig.-6.

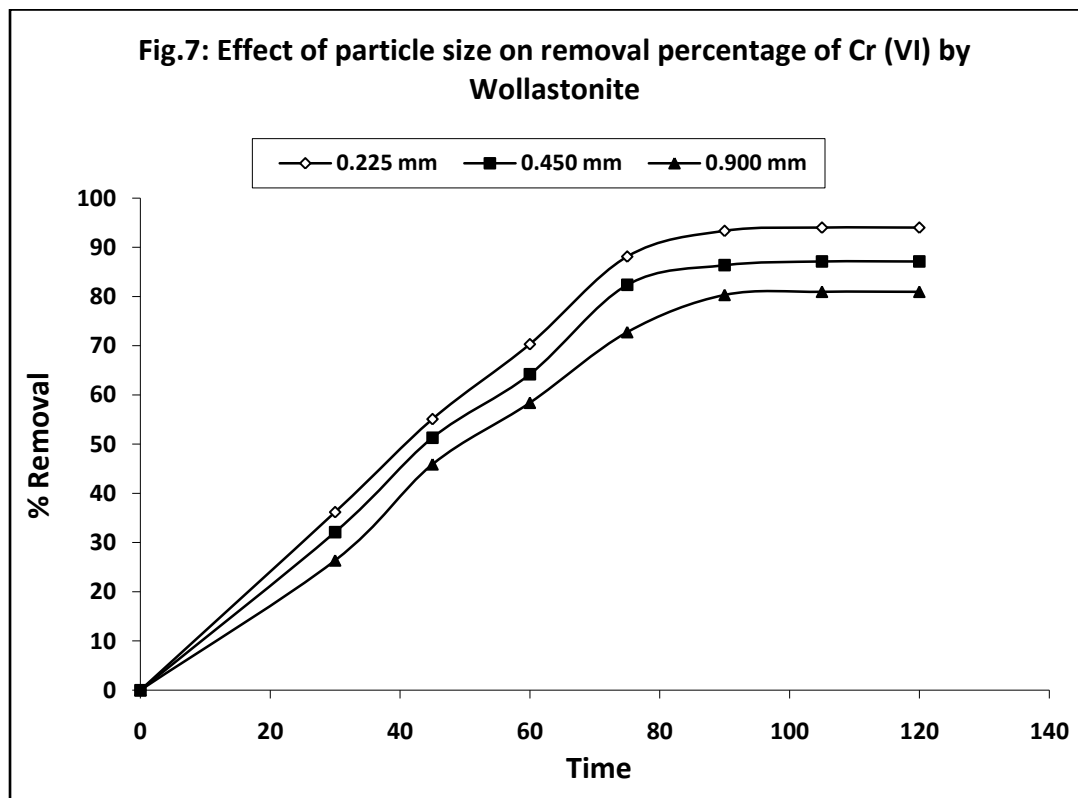


In solution Cr (VI) releases HCrO_4^- at low concentration which readily adsorb on Wollastonite surface. Generally this adsorption readily occurs at pH 1 to 3. The adsorption of Cr (VI) was very slow without agitation or at low agitation speed. When agitation speed increase from 30 rpm to 180 rpm adsorption of Chromium increases at particular initial concentration of Chromium. Maximum and minimum removal of Cr (VI) was found 180 rpm and 30 rpm. In 100 gm/L initial concentration of Chromium maximum and minimum removal percentage was 91.50% to 68.02% in 200 mg/L solution 85.01% to 65.09% and in 400 mg/L 80.12% to 61.29%. After 100 rpm agitation removal of Cr (VI) approximately achieved equilibrium. It can be explain on the basis of interaction between adsorbent and adsorbed particle which attributes to the decrease in boundary layer thickness around the adsorbent particle being a result of increasing the degree of mixing¹⁸.

Effect of particle size on removal percentage of Cr (VI)

Commercial Wollastonite consists of different size of particle used in experiments. It observed that different particle size of adsorbent adsorb different amount of adsorbate. Smaller particle size of Wollastonite gave better Cr (VI) removal because smaller particle size provides larger active surface area for adsorption per unit mass of adsorbent when it

compared with larger particle of Wollastonite. Particle size 0.225mm at initial concentration 100 mg/L, 35°C 100rpm agitation removed Cr(VI) 36.20% in 30min, 55.10% in 45 min, 70.32% in 60 min, 88.13% in 75 min and 93.35% in 90 min. The removal of Cr (VI) decreased at same parameter when performed 0.450mm particle size of Wollastonite.



Maximum and minimum removal of chromium on 0.450mm particle size was found 87.13% to 32.18% with bigger particle size minimum and maximum removal percentage was found 26.37% to 80.96%¹⁹. In smaller particle size of Wollastonite, number of active adsorption site increase and higher removal percentage of Cr (VI) is observed²⁰. Small particle of wollastonite came in more contact of adsorbate as compared to larger particles. The electrostatic forces decreases as particle size of wollastonite increases which influence removal percentage of chromium.

Conclusion

It is concluded that in low initial concentration of chromium in the presence of high adsorbent dose removed maximum Cr(VI). Adsorption of chromium is proportional to the availability of active free adsorption site on wollastonite. Cr(VI) adsorption is attained an



equilibrium passing to all affecting parameters such as pH, contact time, agitation of reaction mixture and particle size of wollastonite. Equilibrium of adsorption process may after when affecting parameter change. Minimum and maximum removal of chromium is co-related with different adsorption parameters.

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