

Studies of Modified bentonite for Removal of Cr(vi) from Aqueous Medium

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ABSTRACT

Hexavalent chromium has been established as a human carcinogen through the route of water and air. This paper deals with the low cost and eco-friendly method of removal of Cr(VI) from aquatic environment using modified Bentonite. Bentonite having Montmorillonite unit with 2:1 octahedral structure, have emerged as an alternative to traditional methods. The ratio of SiO₂ and AlO₃ in bentonite composition is 4.125 having minor oxides of K, Na and Mn. Loss on ignition is 8.87% which resembles montmorillonite. Kinetic studies have been done by treating modified bentonite with FeCl₃ solution with 100 ml 2 ppm Cr(VI) solution up to different intervals of time. Plot of C_t/q_t Vs C_t indicates that Langmuir adsorption isotherm is followed. A plot of adsorbed amount Vs time shows that first order kinetics is obeyed. The removal percentage of Cr(VI) at pH 2,4 and 8 are 60.8, 70.5 and 55 respectively. The optimum pH for the removal of Cr(VI) is 4. Stacks of layers and aggregates in SEM images explain greater surface area for adsorption.

Key words: Carcinogen, Modified bentonite, SEM images, Cr(VI), Langmuir adsorption isotherm.

Introduction

Amongst different oxidation states of Cr(VI), Cr(III) and Cr(0), Cr(VI) has been established as a carcinogen causing adverse health effects to human and aquatic environment (Pang *et al.*, 2014; Mclean *et al.*, 2012; Jha, 2014). The entry pathway of toxic heavy metals including chromium may be explained as occurring due to mining operations, dyeing, lather tanning and petrochemical industries. Several traditional methods of removal of heavy metals, i.e. chemical precipitation, ion exchange and adsorption by agricultural solid wastes are available (Majumder and Jha, 2020; Jha and Kumar, 2020; Jha *et al.*, 2021) In addition, aquatic weeds (Jha *et al.*,

2015; Jha and Kumar, 2017) bacterial biomass, tree leaves, sawdust, orange peel powder, microorganisms used in the bio filtration method, fungal biomass and biomass of walnut, hazelnut have also been found suitable for remediation of Cr(VI) (Srivastava and Majumder, 2008; Pehlivan and Altun, 2008). But here in this paper, removal of Cr(VI) by modified bentonite has been utilized with a view to devise low cost method of removal. Bentonites are smectite group of mineral having montmorillonite unit with 2:1 dioctahedral structure (Jha and Mishra, 2012). Three dimensional network of AlO₄ and SiO₄ tetrahedrally linked to each other by sharing through oxygen exists. Isomorphic substitution of cations in the crystal lattice results in a net negative

structural charge. Naturally occurring bentonites have a wide number of industrial applications e.g. drugs, plasticizers, adhesives, cosmetics, colour adsorbents and wine refining (Jha, 2018). The presence of montmorillonite unit is confirmed by after treatment with benzidine solution. Owing to its good cation exchange capacity, these are used as remover of a number of unwanted cations in aqueous environment. Clay minerals in general acts as a natural remover of pollutants by taking up toxic cations and anions.

The cation exchange capacity may be shown as
 $BH + M^+ = BM + H^+$

Where M^+ is cation, H^+ is cation. M^+ exchange H^+ cation and so BH is an exchanger.

Bentonite minerals of Raj Mahal hills have high cation exchange capacity and as a result these have been exploited for defluoridation, removal of heavy metals from aqueous medium and softening of hardwater thus exhibiting great utility (Jha *et al.*, 2011).

The composition of bentonite minerals have mainly oxides of silicon, aluminium and iron which can be shown as

Oxides	Composition(%)
SiO ₂	62.58%
Al ₂ O ₃	15.17%
K ₂ O	2.11%
Na ₂ O	1.62%
CaO	0.15%
MgO	0.20%
Fe ₂ O ₃	5.15%
P ₂ O ₅	0.12%
MnO	0.83%
LOI(loss on ignition)	8.87%

Bentonites have been characterized by TGA, DSC and PXRD studies and published (Jha, 2016). SiO₂, Al₂O₃, Fe₂O₃ are present as major oxides whereas TiO₂, P₂O₅, Na₂O, K₂O, CaO and MgO are present as minor oxides (Gupta *et al.*, 2011).

Modified bentonites chemically treated with NaCl solution and other surfactants have been found to possess good adsorption potential (Majumder *et al.*, 2020; Jha and Majumder, 2020). and adsorption capacity can be enhanced by modification with several substances. Interlayer surfaces of montmorillonite, majority of which is present in bentonite, absorb water molecules and intercalation of bentonite takes place by organic compounds, surfactants and inorganic compounds too (Zohra *et al.*,

2014).

Though several adsorption isotherms are available, Freundlich and Langmuir isotherms are usually employed to explain nature of adsorption. Freundlich isotherm refers to multilayer adsorption whereas Langmuir isotherm refers to monolayer adsorption. When C_t/q_t is plotted against C_t , Langmuir isotherm is obtained whereas a plot of $\log q_t$ versus $\log C_t$ gives Freundlich isotherm. $q_t(x/m)$, the mass of adsorbate per unit mass of adsorbent is calculated as:

$$q_t = (C_o - C_t/w) \times V.$$

where w is the mass of adsorbent, V is the volume of solution in litres. Percentage removal is calculated as

$$\% \text{removal} = (C_o - C_t/C_o) \times 100$$

Where C_o represents initial concentration and C_t represent concentration at t time.

Materials and Method

Composition of natural bentonite

SiO₂ percentage has been determined from UV-Vis Spectrophotometer. Na and K has been determined from Flame Photometer. Al, Fe and Zr have been determined from ICP-OES analyzer Perkin Elmer Avio 560Max.

Preparation of modified bentonite

An aqueous solution of 0.1 M NaOH is added to a 0.1 M FeCl₃ solution to obtain 0.1 mol L⁻¹ FeCl₃ solution. This solution is slowly added to bentonite clay powder principally Na- montmorillonite and allowed to stand for 24 hours. The product is filtered and washed with double distilled water to make it free from traces of chloride. The solid thus obtained is dried at 100 °C and pulverized to 300 mesh sieve. Clays thus intercalated with iron oxide show high surface area and microporous structure are obtained on heating.

100 ml 2 ppm Cr(VI) solution is treated with 1gm modified bentonite upto 30 min, 60 min and 120 min separately in 250 ml conical flask at a room temperature of 26 °C and further 2 g and 3 g bentonite powder are treated with 100 ml 2 ppm Cr(VI) solution upto 1 hour. The residual concentration of Cr(VI) is measured from the solution by U.V. double beam Spectrophotometer Pharo 300.

Results and Discussion

FTIR

Fig. 1 explains the FTIR peaks of the sample. The peaks are 3618.12cm^{-1} , 3392.3cm^{-1} , 1634.43cm^{-1} , 1219.84cm^{-1} , 990.8cm^{-1} , 772.57cm^{-1} , 441.31cm^{-1} , 520.17cm^{-1} , 1210.8cm^{-1} , 1034.4cm^{-1} , 466cm^{-1} and 430cm^{-1} .

The band at 3700 cm^{-1} and 3725 cm^{-1} show the presence of OH⁻ layer. Peaks at 785 cm^{-1} show Mg-O bond. The peak around 978.2 cm^{-1} shows Al-O bond. 1219 cm^{-1} peak shows Si-O bond similar to montmorillonite.

SEM images for Bentonite

SEM images show grains from several to tens of in size. Grains exhibit a porous and spongy texture obtained from FE-SEM apparatus which facilitate adsorption. Morphological features describes clay structure of smectite type (Iriarte *et al.*, 2005; Landeros *et al.*, 2013). Some grains resemble stacks of layers, aggregates. A highly compact structure formed by small curved or bent layers provide large surface resembling to that of smectites.

Effect of contact time

The contact of the modified bentonite with 100 ml 2 ppm Cr(VI) solution is very significant in removal of Cr(VI) in view of making available more number of adsorption sites with increasing time (Wang *et al.* 2022; Korde *et al.*, 2022). A number of adsorption experiments have been carried out at a time interval of 30 min, 60 min, 90 min, and 120 min keeping the initial concentration at 2 ppm. Table 1 and 2 clearly show that optimum time for maximum removal is 90 minutes at a pH of 4. Table 3 indicates the amount of Cr(VI) adsorbed with different adsorbent

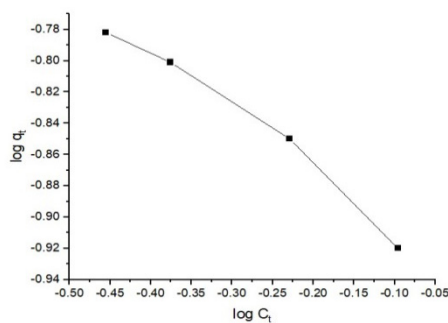


Fig. 2. $\log q_t$ Vs $\log C_t$

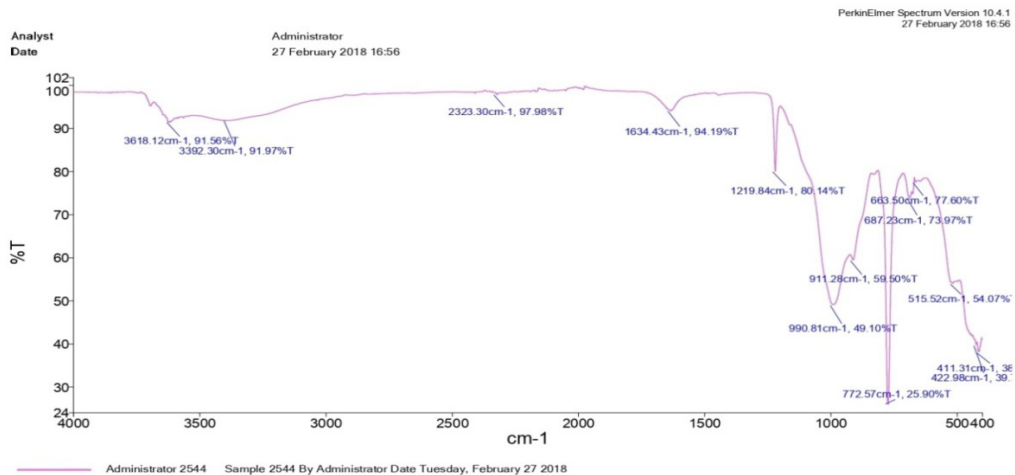


Fig. 1. FTIR peaks of T4(Bentonite)

Table 1. Effect of contact time on removal of Cr(VI) by 1g modified bentonite at pH4.

Time in Minutes (C_t)	Residual Concentration	Cr(VI) absorbed	q_t	C_t/q_t	$\log q_t$	$\log C_t$
30	0.8	1.2	0.12	6.67	-0.920	-0.096
60	0.59	1.41	0.141	4.184	-0.850	-0.229
90	0.42	1.58	0.158	2.65	-0.801	-0.376
120	0.35	1.65	0.165	2.12	-0.782	-0.455

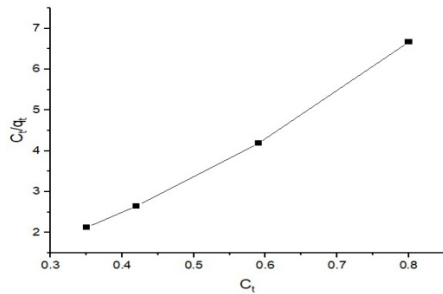


Fig. 3. C_t/q_t Vs C_t

dosage. Fig.5 explains the maximum adsorption at pH 4. Fig. 4 reveals that adsorption obeys first order kinetics and at 120 minute some release or desorption takes place.

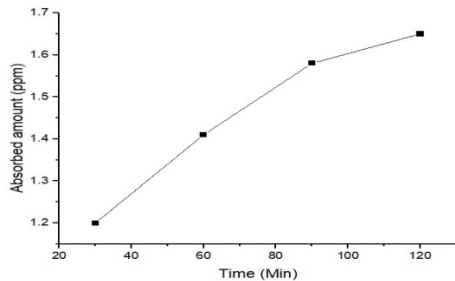


Fig. 4. Adsorbed amount (ppm) Vs Time (Min)

Table 2. Effect of pH on removal of Cr(VI) by modified Bentonite

pH	Percentage removal
2	60.8
4	70.5
8	55

Effect of the adsorbent dose

A number of experiments have been carried out by varying the dose of modified bentonite upto 1 hour. The adsorbent dose varies from 1 g to 3 g. It has been noticed that with increased dose adsorption increases due to increased surface area of adsorbent

Table 3. Effect of adsorbent dose on removal of Cr(VI) at pH4 upto 1 hour

Weight of modified Bentonite	Residual concentration (ppm)	Cr(VI) adsorbed (ppm)
1g	0.59	1.41
1.5g	0.50	1.50
2g	0.41	1.59
3g	0.62	1.38

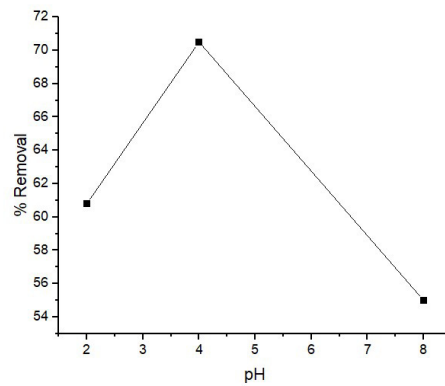


Fig. 5. % Removal Vs pH

(Sahu *et al.*, 2022; Guo *et al.*, 2022). But noticeable change has not been observed with 3 g of modified bentonite. Rather it appears that some release takes place. Fig. 6 clearly explains the release of Cr (VI) with increased dose of modified bentonite.

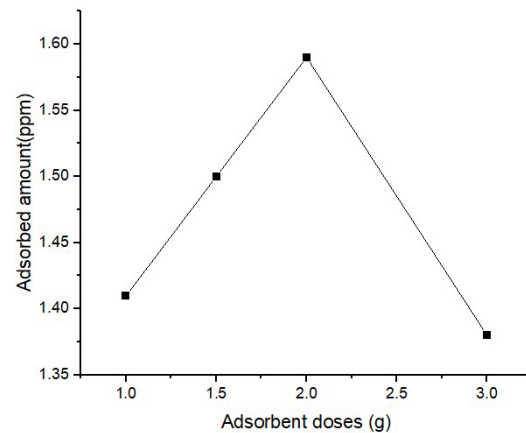
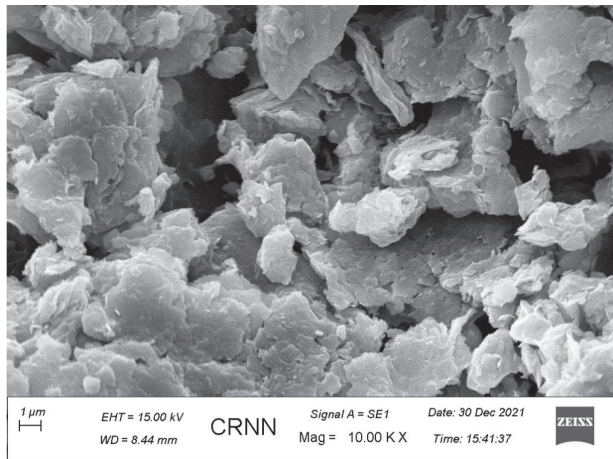


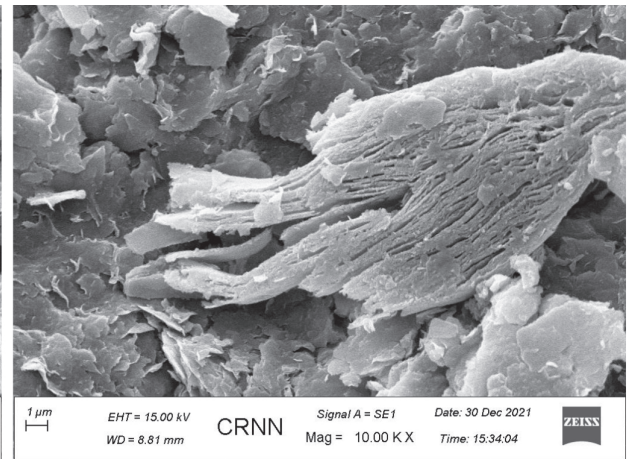
Fig. 6. Adsorbed amount of Cr(VI) (ppm) Vs Adsorbent doses of modified bentonite (g)

Effect of pH

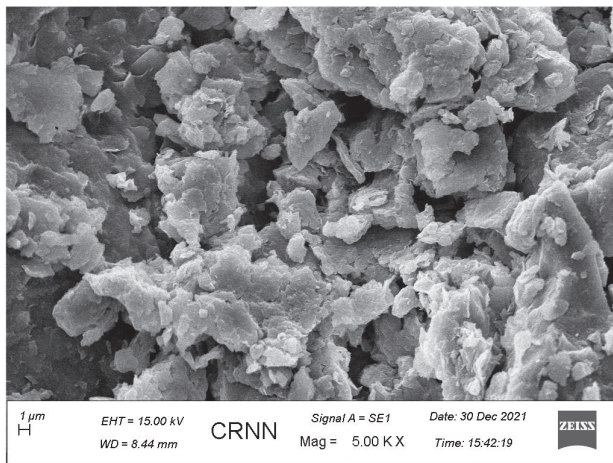
The removal of Cr(VI) from aqueous solution is pH dependent shown by experimental findings (Ordinartsev *et al.*, 2022). It has been observed that maximum adsorption of Cr(VI) takes place at pH 4. The percentage removal at pH 7 is reduced upto 55 % whereas at pH 2 removal percentage is 60.8. Lower pH and higher pH does not facilitate adsorption of $Cr_2O_7^{2-}$, $HCrO_4^-$ and CrO_4^{2-} . In alkaline pH, there is a competition between OH^- and CrO_4^{2-} as a result more OH^- remains on the surface. But at pH 4, the surface of the modified bentonite remains positive and more $HCrO_4^-$ is adsorbed. Adsorption of



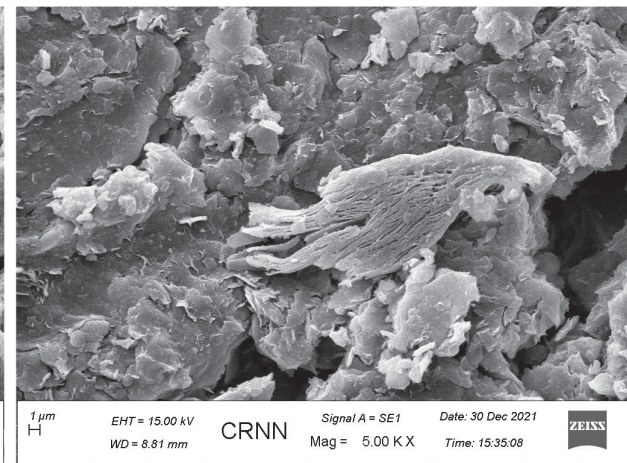
(a) T4-01SEM image of Bentonite before adsorption at 10KX



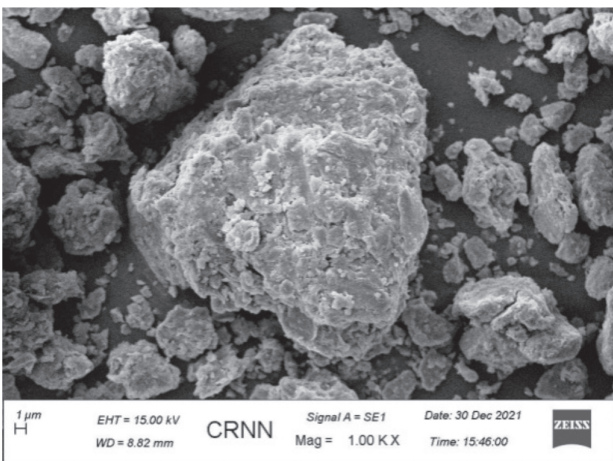
(b) T3-01SEM image of bentonite after adsorption at 10KX



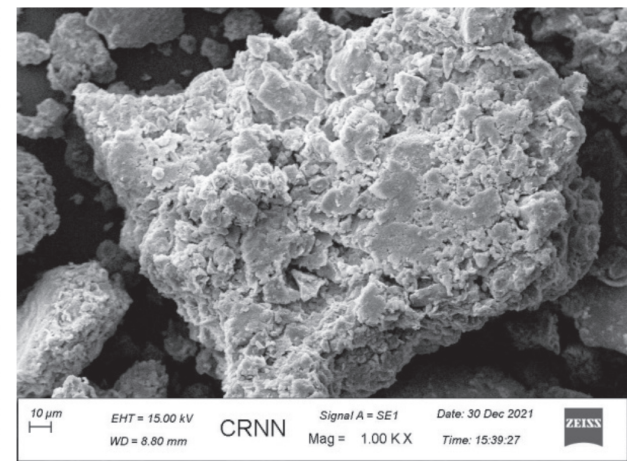
(c) T4-02SEM image of bentonite before adsorption at 5KX



(d) T3-02SEM image of bentonite after adsorption at 5KX



(e) T4-06SEM image of bentonite before adsorption at 1KX

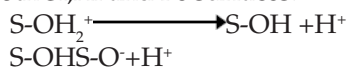


(f) T3-06SEM image of bentonite after adsorption at 1KX

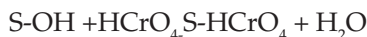
Fig. 7. SEM images of before and after adsorption

Cr(VI) may be explained to take place by mechanism given below.

Let the active surface sites of modified bentonite for both Si, Al and Fe surfaces.



S-OH₂⁺ be the protonated surface functional group and S-OH neutral group. The pH-dependent Cr(VI) adsorption may be shown by equation given below.



Adsorption Isotherm

A plot of log q_t Vs log C_t in Fig. 2 explains Freundlich isotherm leading to multilayer adsorption whereas a plot of C_t/q_t Vs C_t in Fig. 3 explains Langmuir isotherm. The linearity obtained in the plot of C_t/q_t Vs C_t clearly shows that Langmuir isotherm is being followed.

The linear graph of C_t/q_t Vs C_t clearly shows that Langmuir isotherm adsorption is being followed indicating monolayer adsorption

SEM image

Grains shown in images resemble stacks of layers and aggregates. A highly compact structure formed by small curved or bent layers provide large surface area very similar to smectite (2:1) dioctahedral structure (Wang *et al.*, 2022; Kumar *et al.*, 2022). Figure 7 (a)-(f) of SEM images before and after adsorption clearly explain adsorption of Cr(VI) on modified bentonite surface.

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