



SORPTION OF CHROMATE BY SURFACTANT MODIFIED WILLHENDERSONITE

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(Received : 02.09.2011; Revised : 12.09.2011; Accepted : 15.09.2011)

ABSTRACT

A new sorbent, ordered mesoporous surfactant modified Willhendersonite, was prepared and applied for the sorption of chromate from water. The sorbent showed higher efficiency for the sorption of Cr (VI). The maximum uptake at pH 7.0 was 80 mg g⁻¹ for Cr (VI). The behaviour of Cr (VI) sorption onto surfactant modified Willhendersonite was investigated by sorption isotherms, sorption kinetics and the effect of pH on sorption. The sorption equilibrium of chromate was rapid, with 90% sorption in 7 hours. The surfactant modified willhendersonite was characterized by using FTIR, XRD, TEM, SEM, DTA/TGA and E-DAX techniques.

Key words: Willhendersonite, Cr (VI), FTIR, XRD, TEM, SEM, DTA/TGA and E-DAX.

INTRODUCTION

Chromium is an ubiquitous element, not only because of its occurrence in nature, but also due to the many anthropogenic sources resulting from its widespread industrial application¹. Chromium and its compounds are used in refractories, drilling mud, electroplating cleaning agents in the metal finishing industry, mordants in the textile industry, catalytic manufacture, fungicides and wood preservatives, in the production of chromic acid and specialty chemicals. Other uses for chromium and its compounds include organic chemical synthesis, leather treatment, photomechanical processing and industrial treatment, including treatment of cooling tower water². As chromium is very widely used, there are many sources of leaching the chromium into the natural water system and it should be removed practically.

Cr (VI) is toxic and a carcinogenic. It is quite soluble in the aqueous phase almost in the entire pH range and mobile in the natural environment. The carcinogenicity and toxicity of Cr (VI) is based on its state where the chromate anion resembles the form of sulfates and phosphate³. In addition, the toxic nature of the Cr (VI) ions is attributed to their high oxidation potential and their relatively small size, which enables them to penetrate through biological cell membranes⁴. In contrast, Cr (III) does not resemble any biological nutrient and has no similar way to enter the cell. However, it is possible that Cr (III) may be oxidized into Cr (VI) in the appropriate condition, hence the toxicity of Cr (VI) take place. Usually, Cr (III) is readily oxidized to the hexavalent state at high pH⁵. Presently, Cr (VI) has been recognized as a probable agent of lung cancer and it also produces gastrointestinal disorders, dermatitis and ulceration of skin in man⁶.

The regulation for the limitation of the chromium concentration in water should be highlighted and emphasized in every country due to the toxicity, reactivity and probable carcinogens of chromium.

Acceptable limits for the chromium in water differ in almost every country. As a guideline, the World Health Organization (WHO) recommends a maximum level of 50 $\mu\text{g/L}$ (ppb) for Cr (VI) in drinking water⁷ and the National Institute for Occupational Safety and Health (NIOSH) recommends that the levels of chromium should be reduced to 10-3 mg/m^3 .⁸ The Environmental Protection Agency (EPA) has set the MCL (Maximum Contaminant Levels) at 0.1 ppm in drinking water because EPA believes, given the present technology and resources, this is the lowest level where the removal of this contaminant can be achieved in drinking water.

The sorption of Cr (VI) on various sorbents has been studied extensively as an alternative process for removing Cr (VI) from water solutions. The activated carbon is the most studied sorbent and his capacity for sorbing Cr (VI) is dependent upon the solution pH. In the last years the sorption of Cr (VI) on several low cost biosorbents has been investigated⁹.

Zeolites are based on an infinitely extending three dimensional network of AlO_4 and SiO_4 tetrahedral linked to each other by sharing all the oxygen ions¹⁰. The most naturally occurring materials have negative charges on their external surfaces, which will prevent sorption and retention of anions, efforts were made to convert the surface charges from negative to positive by surface modification to increase their anion retention¹¹ due to strong sorption on negatively charged materials, cationic surfactants were used extensively for modification of clay minerals and zeolite¹²⁻¹⁴. The surfactant-modified zeolite were initially intended as sorbent to remove hydrophobic organic compounds from water because of their higher organic carbon contents after modification. Subsequently, researchers found that in the presence of surfactants (i.e. beyond 100% of external cation exchange capacity of zeolites). The sorbed surfactant molecules from an admicelle formation, resulting in strong sorption of anionic contaminants such as arsenate and nitrate¹⁵.

The primary objectives of this study were: (1) To determine the maximum HDTMA sorption level by modified willhendersonite. (2) To mdified the willhendersonite with HDTMA to thesorption plateau and use the modified zeolite to study the sorption of anionic contaminants. (3) To investigate the relationship between HDTMA sorption and contaminant sorption. (4) Furthermore, the sorption behaviour of Cr (VI) on surfactant modified willhendersonite was elucidated by fourier transform infred (FTIR) spectroscopy.

EXPERIMENTAL

Sample preparation (Synthesis of Willhendersonite)

To synthesize analogues of willhendersonite $\text{KCaAl}_3\text{Si}_3 \cdot 25\text{H}_2\text{O}$, the metalion potassium, calcium, aluminium and silicon were taken in the molar ratio 1 : 1 : 3 : 3, respectively. They are used as their salt potassium nitrate, calcium nitrate, aluminium nitrate, tetra aminosilicate.

The materials were synthesized by taking homogeneous solution of their respective salts prepared in doubly distilled water, the solutions were thoroughly mixed and after homogenization the precipitate formed was autoclaved for 72 hours in a Teflon lined stainless steel pressure vessel of PARR make in an oven at 200°C. After hydrothermal treatment the content were filtered and washed with distilled water and dried.

Modification of Willhendesonite

To synthesized the analogue of willhendersonite, the synthetic raw willhendersonite were treated hexadecyltrimethylammonium bromide (HDTMA-Br) surfactant at a level 150 mmol/Kg (42.6 HDTMA per kg of Willhendersonite). Each mixture was equilibrated on a water bath shaker at 150 rpm and 250°C for 8 hours. Then mixture was centrifuged and the supernatant solution analyzed. Zeolite were washed with to portions of type I distilled water and then air-dried.

Characterization

Powder X-ray diffraction analysis was performed on an X-ray diffractometer with $\text{CuK}\alpha$ radiation at 45 kV and 40 mA. XRD patterns of randomly oriented samples were collected from 2θ equal to 5° to 70° at the scanning rate of $2^\circ/\text{min}$ using 1° divergent slit and scatter slit and 0.3 mm receiving slit, while those of oriented samples were collected from 2θ equal to 5° to 50° .

FTIR spectra of HDTMA modified willhendersonite were recorded on a FTIR spectrometer (NICOLET 410 Spectrometer).

Thermogravimetric analysis was performed on Perkin Elmer (Pyris diamond) in the temperature range of $25\text{-}900^\circ\text{C}$ for zeolite product with a heating range of $10^\circ\text{C min}^{-1}$ under flowing air.

Batch sorption tests

Sorption isotherm were conducted by batch experiments at 20°C , pH 7.0¹⁸. The experiments were carried out in 150 mL stoppered conical flasks containing 100 mL of chromium (potassium chromate K_2CrO_4 , AR) solutions with concentration $1\text{-}35 \text{ mg L}^{-1}$, with sorbent 0.1 g L^{-1} . To analyse the effects of pH, the equilibrium sorption of chromium measured at different pH levels from 3 to 10 by setting the initial chromate concentration at 5 mg L^{-1} with sorbent 0.1 g L^{-1} . The initial pH of solution was adjust by 0.1 M HCl and NaOH solutes. The flasks were shaken at 180 rpm in a shaker for 24 hours and then the suspension was passed through a membrane filter ($0.45 \mu\text{m}$) for analysis. Chromate was analysed on an UV-Spectrophotometer (Systronic). Experiment were repeated three times, and all of the data are the average of the three. Kinetic study was consulted reference¹³. Kinetic studies were carried out for different time periods, using buffer solution pH 7, in 2 hours time intervals (1, 3, 5, 7- - - 9h), according to the above procedure for different concentrations. The initial chromium concentration was 10 mg L^{-1} , the sorbent was 1 g L^{-1} , and the initial pH was 7.0.

RESULTS AND DISCUSSION

Characterization of the sorbents

XRD study of materials

Analogues of modified Willhendersonite with different degrees of crystallinity and crystal size (determined by XRD) were obtained in the experiments. Powder X-Ray diffraction patterns of these analogues synthesized from media of NaOH concentration and with sodium silicate as the silica source are shown in Fig. 1. In this case, the degree of crystallinity is very high.

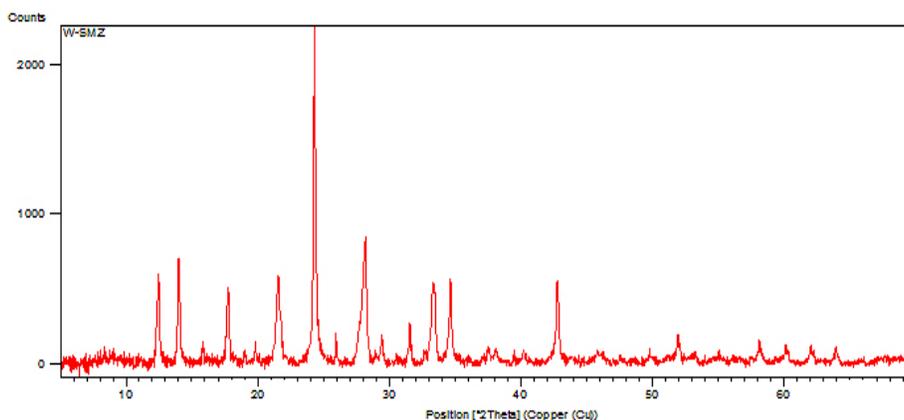


Fig. 1: XRD diffractogram of surfactant modified Willhendersonite

Powder X-Ray diffraction pattern for Willhendersonite material was recorded at room temperature on PW 3064 diffractometer. Samples were scanned using CuK α radiation of wavelength (λ) = 1.54060 Å and the diffractograms were recorded in the range $2\theta = 5^\circ - 70^\circ$ at the scanning speed of 1 step/second^{16,17}.

Powder X-Ray diffraction (XRD) patterns were taken after different hydrothermal crystallization periods. While using the silica source and maintaining the same temperature and stirring conditions as given in Fig. 1. It shows sharp peaks which indicate the crystalline nature of synthesized materials.

SEM study of materials

The morphology and crystal size of the synthetic material was examined by scanning electron microscopy (SEM). Samples were analyzed by using Ametek Advanced Microscope and the imaged obtained shows the morphology of the materials.

Powders of the sample and coated surface were characterized to obtain information about the size and morphology using scanning electron microscope, which provides topological and elemental information about the sample¹⁸.

The SEM images (Fig. 2) of the synthetic modified willhendersonite show various morphologies of the mesostructured materials depending on the crystallization conditions. Photomicrographs of the synthetic modified Willhendersonite exhibited well defined narrow shape with excellent crystal edges.

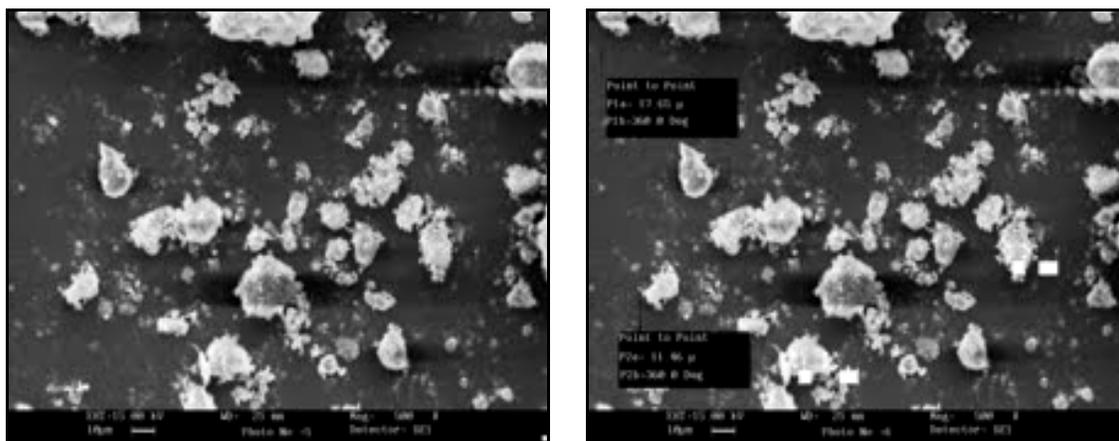


Fig. 2: SEM Micrographs of surfactant modified gel Willhendersonite

TEM study of material

The very small size of synthesized material can be determined more easily with TEM rather than SEM. Another reason to perform TEM study is its ability to resolve and show individual particles clearly in an aggregation of particle mass. TEM analysis was carried out by HITACHI microscope using a tungsten filament source and accelerating voltage of 120 KV. Sample was made by suspending material in distilled water, consequently by loading onto 300-mesh copper grid.

In the TEM micrograph (Fig. 3) of synthesized Willhendersonite ~10-20 nm sized particles are observed, which indicate crystalline nature of the synthesized material. TEM studies confirm that the nature of synthesized medium and other synthesis parameters have large impact on the crystal morphology. The TEM and XRD result are in good agreement and indicate that the materials have ordered microporous crystals.

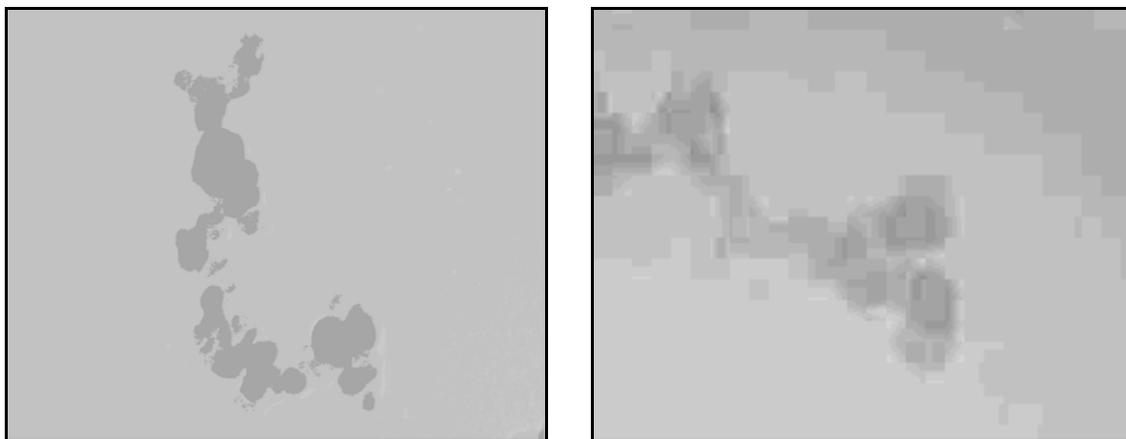


Fig. 3: TEM Micrographs of hydrothermally synthesized and modified gel Willhendersonite

DTA / TGA study of materials

Thermal stability and the number of water molecules bound with the synthetic modified analogues of Willhendersonite were ascertained by thermo gravimetric analysis. TGA data were recorded on Perkin Elmer Thermobalance with alumina crucible and alumina powder reference. The heating profile consisted of 20°C/min up to desired temperature (900°C).

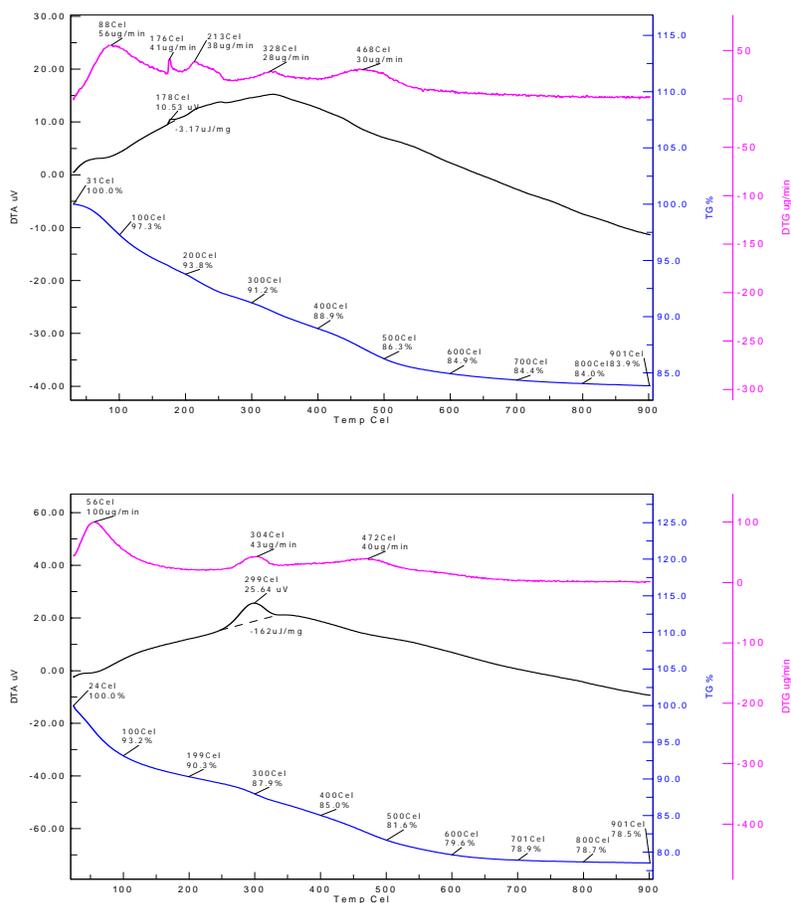


Fig. 4: TGA/DTA graph of surfactant modified Willhendersonite

Thermogram of synthesized modified Willhendersonite gel (Fig. 4) shows 15.0% weight loss between 25°C to 400°C, which also probably correspond to dehydration and sorption of the physically sorbed water molecules, then 7.1% weight loss in the temperature range 400°C to 700°C, which correspond to carbonate and anhydrous form of gel and then up to 900°C the thermogram shows the structural stability.

FTIR study of materials

The organo-zeolites, in contrast to unmodified zeolites, have two intense bands around 2850 cm^{-1} and 3500 cm^{-1} , which are assigned to asymmetric and symmetric stretching vibration of C-CH₂ of the alkyl chain, respectively.

The intensities of these peaks increased with increasing surfactant loading. The structure sensitive bands (400 -1200 cm^{-1}) are not affected by the surfactant treatment. The strong band appearing at around 1250-1400 cm^{-1} due to the bending mode of water is weaker for the organo-zeolites than for unmodified zeolites. The weakening of this band can be ascribed to an intensification of the hydrophobic characteristics of the organo-zeolite samples, which is in agreement with the result for the sorption of water vapour. It was found that there was a strong peak between 900-1700 cm^{-1} , which was absent in unmodified analogue of zeolite that is attributed to N-Br bond in the modified zeolite by hexadecyltrimethylammonium (HDTMA) is given in Fig. 5.

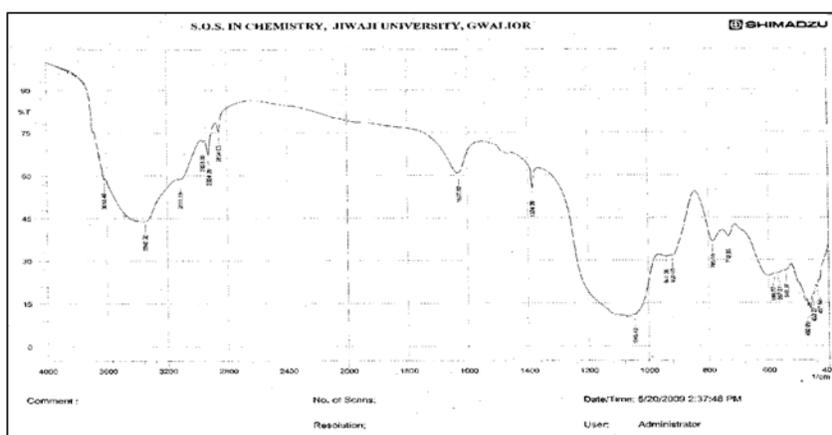
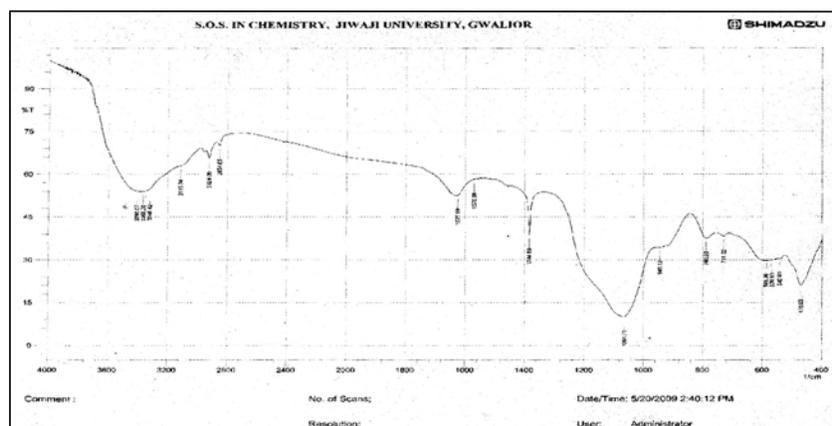


Fig. 5: FTIR Spectrum of surfactant modified gel Willhendersonite

EDS study of materials

EDS analysis show very high Si/Al ratio to that of initial composition of these metals taken for synthesis of Willhendersonite analogues, which means aluminium in these cases remain un reacted and wash out from the material surface during washing.

The weight % of metal ions estimated for Na, Ca, Al and Si agree very well with the weight % of these metal ions on the basis of their amount taken.

The EDS graph (Fig. 6) of material, suggest that hydrothermal product is close to Willhendersonite. Since EDS analysis in terms of Si/Al ratio provide the information on the bulk composition and not on the framework composition, therefore sample were further subjected to other spectroscopic studies.

Sorption kinetics

Kinetic study for the sorption of CrO_4^{2-} , on the surface modified willhendersonite have been performed to find out the maximum time for the attainment of sorption equilibrium the studies were performed at 1, 3, 5, 7 and 24 hours. The results obtained suggest that a maximum equilibrium time 7 hours is required to attain the equilibrium. Results are given in Table 1 and Fig. 7. The experiments were carried out by taking the maximum surfactant loading of surface modified willhendersonite. The plots of sorption percentage versus time indicate that sorption become asymptotic to the time axis representing nearly an equilibrium pattern.

Microanalysis report

<i>Element</i>	<i>Wt%</i>	<i>At%</i>
<i>CK</i>	64.97	74.68
<i>OK</i>	21.64	18.68
<i>AlK</i>	05.38	02.76
<i>SiK</i>	07.66	03.76
<i>KK</i>	00.11	00.04
<i>CaK</i>	00.25	00.08
<i>Matrix</i>	Correction	ZAF

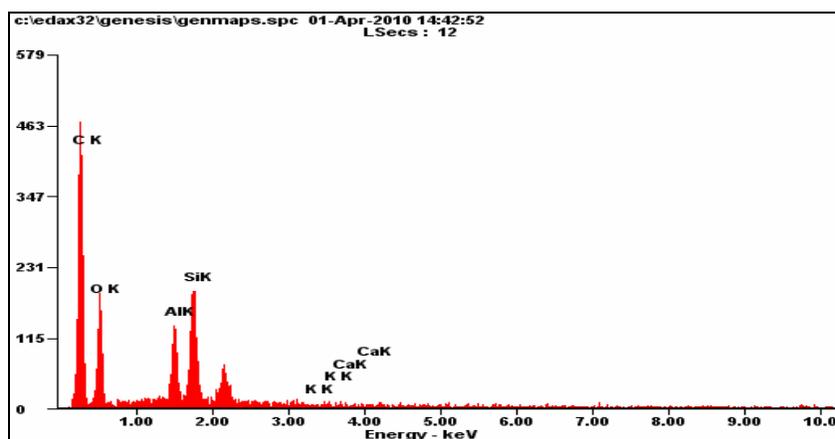


Fig. 6: EDAX graph of surfactant modified gel Willhendersonite

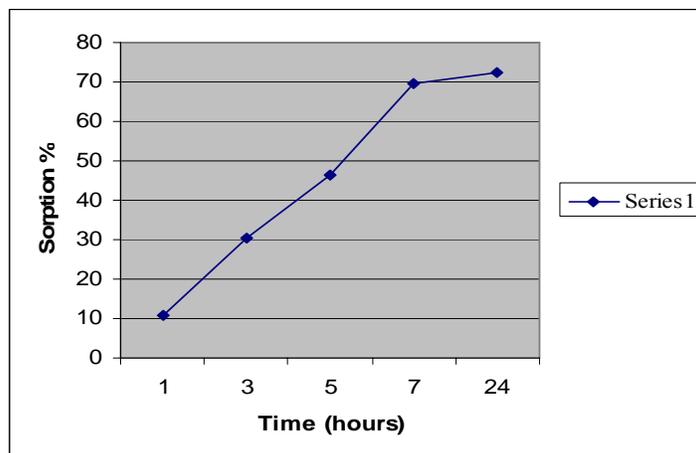


Fig. 7: Effect of time on sorption of metal oxoanions by surfactant modified Willhendersonite

Table 1: Effect of time on sorption of metal oxoanions by surfactant modified Willhendersonite

Weight of ion exchanger = 100 mg

Temperature : 25°C

pH of the solution: 7

Metal oxoanion	Contact time (hrs.)	Initial metal oxoanion conc. meq.	Metal oxoanion conc. in solid phase meq.	Metal oxoanion conc. at equilibrium meq.	K_d mL/gm	Sorption %
CrO_4^{2-}	1	0.5005	0.0545	0.4455	61.16	10.9
	3	0.5005	0.1530	0.3470	220.46	30.6
	5	0.5005	0.2320	0.2680	432.83	46.4
	7	0.5005	0.3490	0.1510	1155.49	69.8
	24	0.5005	0.3615	0.1385	1305.05	72.3

The transient behavior of the batch sorption process at different initial concentrations was analyzed using the Lagergren pseudo-first-order kinetic model and Ho and McKay's pseudo-second-order model. The pseudo-first-order kinetic model, proposed by Lagergren, has been widely used to predict the chromate sorption kinetics. The chromate kinetics following the pseudo-first-order model is given by¹⁹ -

$$\log(q_e!q) = \log q_e - K_1 t/2.303$$

Effect of pH

pH values of 1, 3, 5, 7 and 9 of the CrO_4^{2-} solutions were selected in order to study the effect of pH solution in the sorption of Cr (VI), by surfactant modified Willhendersonite. Table 2 and Fig. 8 show the effect of pH on sorption of metal oxoanions. The data shows maximum sorption at pH 7 for CrO_4^{2-} , AsO_4^{3-} , and SeO_4^{2-} . Results clearly shows that sorption % was directly affected by the pH of the medium and with increase in the pH of the medium sorption % increase and was found to be maximum at pH 7, which may be explained as follows :

In case of chromate (VI) ion maximum sorption occurs at pH 7. Chromium is present in the form of (CrO_4^{2-}), which is more stable form of Cr. However at lower pH, dichromate ions are formed, which has larger particle size as compared to chromate ions. The pore size of zeolite is suitable for the sorption of CrO_4^{2-} ions then the $\text{Cr}_2\text{O}_7^{2-}$ ions.



In the case of basic solution when pH is greater than 7 the chromate ions are converted into Cr (OH)₃ species, it has less oxidizing ability. In case of Cr, +6 oxidation state is more stable as compare to +3 oxidation state therefore chromium shows maximum sorption at pH 7.

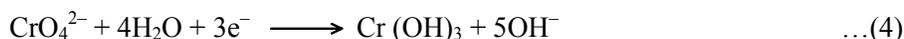


Table 2: Effect of pH of the solution on sorption of metal oxoanions by surfactant modified Willhendersonite

Weight of ion exchanger: 100 mg		Temperature: 25°C			Equilibrium time: 7	
Metal oxoanion	pH of the solution	Initial conc ⁿ of metal oxoanion meq.	Metal oxoanion conc ⁿ in solid phase meq.	Metal oxoanion conc ⁿ at equilibrium meq	K _d mL/gm	Sorption %
CrO ₄ ²⁻	1	0.5005	0.0775	0.4225	91.71	15.5
	3	0.5005	0.1340	0.3660	183.06	26.8
	5	0.5005	0.2170	0.2830	383.39	43.4
	7	0.5005	0.3475	0.1525	1139.34	69.8
	9	0.5005	0.2880	0.2120	679.24	57.6

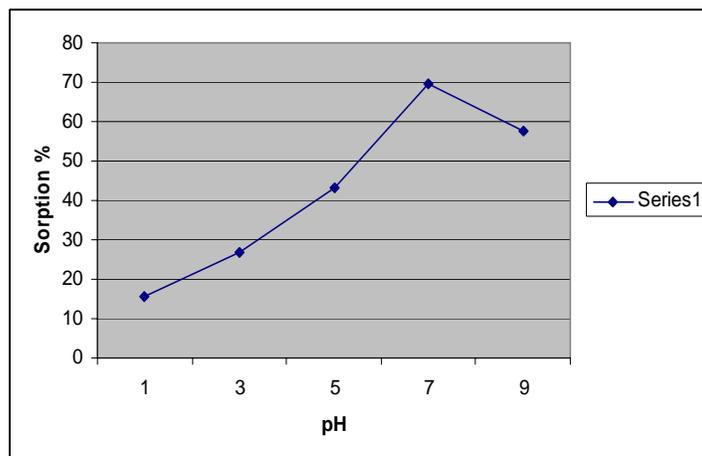


Fig. 8: Effect of pH of the solution on sorption of metal oxoanions by surfactant modified Willhendersonite

Sorption isotherm

Oxyanions are sorbed from aqueous system onto surface of modified zeolite by a wide variety of mechanism. The operative mechanism for any particular reactions depends on the nature and properties of the active sites on the material surface, the bulk chemistry of the system e.g. pH, hydration status, exchangeable inorganic cations and nature of the sorbate. The sorption isotherm is generally used for the design of sorption system. A sorption isotherm was measured using the batch equilibrium method.

Freundlich isotherm model is applied in present sets of the equilibrium data for sorption of metal oxoanions CrO_4^{2-} , AsO_4^{3-} and SeO_4^{2-} by surfactant modified zeolite at 25°C temperature.

Freundlich plot give R^2 values near about 0.9998 for all the sorbents (Table 3) indicating linear relationship between $\log C_{\text{ads}}$ and $\log C_{\text{eq}}$. The sorption is expressed by freundlich equation

$$C_{\text{ads}} = KC_{\text{eq}}^{1/n}$$

Where C_{ads} is the sorbed amount of metal oxoanions, C_{eq} is the equilibrium concentration of metal oxoanion in solution and K and n are the constants which represents sorption capacity and intensity of the sorption. Freundlich exponent $1/n$ provides information about surface heterogeneity and surface affinity for the solute $1/n$ values are computed from slopes of the plots-3.7729. The graph of C_{ads} verses C_{eq} gives a straight line (Fig. 9) for the sorption of metal oxoanions by modified Willhendersonite minerals. The linear graph for these metal oxoanion support the applicability of freundlich isotherm model in case of present study. The values of $\log K$ obtained from the intercept of the groups are given in Table 3. Sorption data of metal oxoanions on modified zeolite minerals fit well in the freundlich isotherm and the values at different temperatures is observed to be linear indicating the applicability of freundlich isotherm model to the sorption of metal oxoanions on these modified zeolite minerals.

Table 3: Sorption isotherm for CrO_4^{2-} sorption on surfactant modified Willhendersonite

Metal oxoanions	Conc ⁿ of metal oxoanions N	25°C		
		$\log C_{\text{ads}}$ (meq/g)	$\log C_{\text{eq}}$ (meq/L)	$\log K$
CrO_4^{2-}	0.01	$\bar{1}.1780$	$\bar{1}.5429$	$\bar{1}.9652$
	0.02	$\bar{1}.5944$	$\bar{1}.7832$	
	0.03	$\bar{1}.8245$	$\bar{1}.9204$	
	0.04	$\bar{1}.9459$	$\bar{1}.9315$	
	0.05	$\bar{1}.7626$	$\bar{1}.8879$	

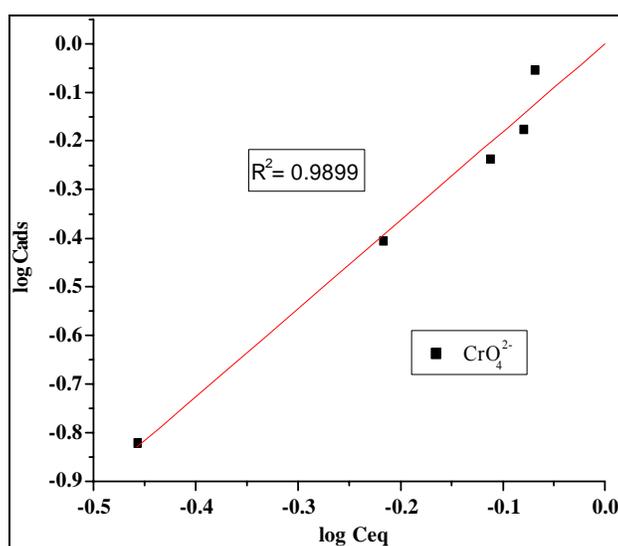


Fig. 9: Sorption isotherm for CrO_4^{2-} sorption on surfactant modified Willhendersonite

Thermodynamic studies

Thermodynamic parameters i.e. free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS), they all vary with the thermodynamic equilibrium constant (K) and were calculated using equation 7, 8 and 9. The negative value of ΔG indicates that the sorption of metal oxoanions on modified zeolite minerals is a spontaneous process. The increase in the numerical value of ΔG with increase in temperature indicates that sorption process become more favorable at higher temperature. The positive value of enthalpy change (ΔH) confirms the endothermic sorption process. The positive value of ΔS suggests the increase in randomness at the solid solution interphase during sorption. Metal oxoanion in aqueous media are hydrated when the anions are sorbed on the sorbent surface, water molecule previously bounded to the metal oxoanions are released and dispersed in solution, resulting in an increase in entropy.

The amount of metal oxoanion sorbed at equilibrium at different temperature has been utilized to evaluate the thermodynamic parameters for the sorption. The Van't Hoff plot of $\ln k_c$ V/s $1/T$ comes out to be straight line Fig. 10 for surfactant modified Willhendersonite respectively.

$$\Delta G^0 = - RT \ln K \text{ or } - 2.303 RT \log K_0$$

$$\log K_2/K_1 = \Delta H^0 / 2.303R [1/T_1 - 1/T_2]$$

$$\Delta S^0 = \Delta H^0 - \Delta G^0 / T$$

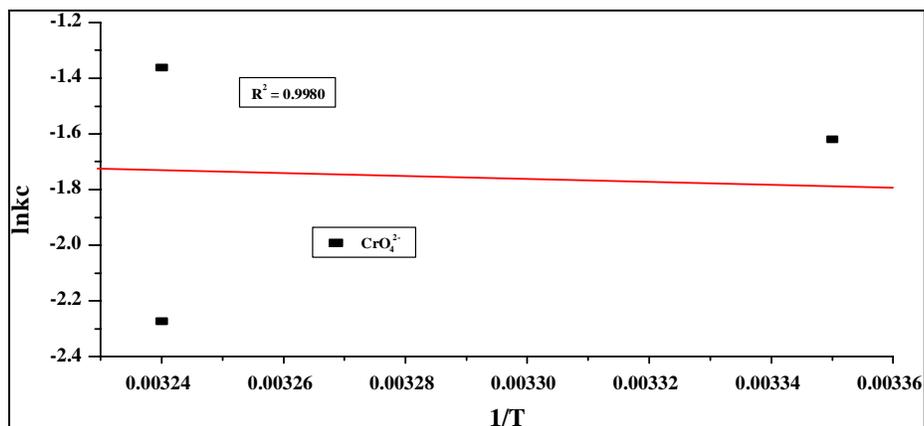


Fig. 10: Thermodynamic parameters for CrO_4^{2-} sorption on surfactant modified Willhendersonite

CONCLUSION

The present study focuses on sorption of Cr (VI) from aqueous solutions using the Willhendersonite-surfactant modified zeolite composite as a low cost sorbent. The sorption characteristic has been examined with the variations in the parameters of concentration of Cr (VI), pH, contact time and temperature. The pH experiments showed that the governing factors affecting the sorption characteristics of sorbent. Sorption is relatively high at pH 7. This phenomenon can be explain by competition of the H^+ ions with chromium ions at low pH values and precipitation of hydroxyl species onto the sorbents (pH 7- 9) at higher pH.

The experimental results were analyzed by using the Freundlich equation. The Freundlich model appears to be the best fitting model for Cr (VI) sorption on the sorbent due to its high regression coefficient, R^2 (0.9899). Also thermodynamic results support this suggestion. Thermodynamic parameters revealed that the sorption process is exothermic and spontaneous with a increased randomness in nature.

ACKNOWLEDGEMENT

The authors acknowledge to Head IIT, IIT Roorkee providing necessary instrumental facilities for XRD, E DAX and TGA analysis and also acknowledge to Head of AIIMS providing facilities for TEM.

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