Analysis of sorption-desorption hysteresis phenomena of chromium in bentonite

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ABSTRACT

Hysteresis or irreversibility has been observed to occur in the sorption and esorption of inorganic contaminants by many soils and sediments under varying environmental conditions. Knowledge of the sorption and desorption of Chromium in the environment can be important for predicting its mobility and threats from its presence. Hence the main objective of this study is to analyse and quantify the sorption and desorption hysteresis phenomenon of Cr III in commonly found clay mineral Bentonite. Batch experiments were conducted for both sorption and desorption under conditions of (i) varying pH from 4-10 (ii) soil solution ratios ranging from 1:60 to 1:100 and (iii) Chromium concentrations ranging from 5mg/l to 30-mg/l with increments of 5-mg/l. Linear and Freundlich isotherms are fitted with curve fitting tool built in MATLAB and best estimated parameters are tabulated for both sorption and desorption stages. Hysteresis indices are developed with Freundlich exponents and the first derivatives of the functions describing the sorption and desorption isotherm branches. Both pH and soil solution ratio have remarkable influence on the irreversibility of Cr III in Bentonite. At higher pH and SSR the irreversibility is less produced and at lower pH and lower SSR the irreversibility is more produced.   © 2008 Trade Science Inc. - INDIA

INTRODUCTION

Chromium is one of the heavy metal that can be hazardous. Contamination of soil and groundwater by chromium is a significant problem and believed to be a long-term threat to the environment. Chromium is a widespread contaminant, typically having been released into the environment as a result of industrial activities such as metal-plating operations, wood preservation, and tanning. It is considered to be an important source of contamination due to large volume of exhaust liquid discharged and solid sludge produced and to its ability to gain access to groundwater and soil, where it has detrimental effects. As a consequence it causes significant pollution both in soil and ground water unless treated in some way prior to discharge[6,23,1].

At sites where such potential risk exists, active remedial measures such as Chemical reduction/fixation

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have been undertaken. Insitu treatment methods for chromium-contaminated soil and groundwater generally involve the reduction of Cr(VI) to Cr (III) with subsequent fixation of Cr(III).

The success of the in situ chromium geochemical fixation technology depends on the ability of the applied reductant to reduce Cr(VI) in groundwater to Cr(III), and on the capacity of the reduced chromium to fix onto the aquifer solids. After effective remediation, chemical parameters within the aquifer, particularly pH, may be altered[22,7,32]. However, to ensure that desorption of Cr(III) will not occur, the remediation site should be characterized to determine how suitable it is for Cr(III) fixation or for other treatment applications[31,27].

Hence an attempt has been made to investigate the Cr(III) sorption and desorption mechanisms under varying environmental conditions like pH, Soil solution ratio and the changing concentrations of Chromium. Batch experiments were conducted with adsorbent Bentonite, which is having unique properties of high CEC and swelling. Higher levels of CEC and clay content increase sorption and inhibit metals contaminant removal. Some degree of "irreversibility or hysteresis" is observed with the corresponding sorption and desorption isotherms. The main objective of this study is to develop Hysteresis Index for quantitative assessment of the degree to the occurrence of desorption of chromium, which alters its environmental mobility. Higher the index, stronger the soil irreversibly binds the contamianant and the potential risk is reduced.

Background

The two major oxidation states of chromium, which occur in the environment, are Cr (III) and Cr(VI). Cr (Vl) exists in solution as monomeric ions $H_2CrO_4^0$, $HCrO_4^-$ (bichromate), and CrO_4^{2-} (chromate) or as the dimeric ion $Cr_2O_7^{2-}$(bichromate). It is the most oxidized, mobile, reactive, and toxic chromium state. In the Cr (III)-H_2O system, Cr (III) exists predominantly as Cr^{3+} below pH 3.5. With increasing pH, hydrolysis of Cr^{3+} yields $CrOH^{2+}$, $Cr (OH)_2^+$, $Cr(OH)_3^0$, and $Cr(OH)_4^-$ (Rai, et al., 1987).

In the Cr (III)-H_2O system, Cr(III) exists predominantly as Cr^{3+} below pH 3.5. With increasing pH, hydrolysis of Cr^{3+} yields $CrOH^{2+}$, $Cr (OH)_2^+$, $Cr(OH)_3^0$, and $Cr(OH)_4^-$[26]. At high concentrations, these ions impart a green color to the solution. Under slightly acidic to alkaline conditions, Cr(III) can precipitate as an amorphous chromium hydroxide. In contrast to the numerous pathways for the reduction of Cr(Vl), there are very few mechanisms for the oxidation of Cr(III). Only two constituents in the environment are known to oxidize Cr(III) to Cr(Vl): dissolved oxygen and manganese dioxides (MnO_2)[10].

Industrial applications most commonly use chromium in the Cr(VI) form, which can introduce high concentrations of oxidized chromium (chromate) into the environment. Cr (VI) does not always readily reduce to Cr(III) and can exist over an extended period of time. The goal of geochemical fixation technology is to reduce Cr(VI) in groundwater and contaminated soil to the more thermodynamically stable Cr(III) with the help of reductants provided there are sufficient iron and manganese oxide adsorption sites within the aquifer treatment zone to which the Cr(III) can affix[22]. The reduced chromium is expected to geochemically fix onto aquifer solids thereby reducing chromium in groundwater.

The success of geochemical fixation treatment techniques is based on forming insoluble non-reactive chemical species. Precipitation and adsorption result in fixation or solid-phase formation of Cr(III), each depending on the physical and chemical conditions existing in the aquifer system. Aquifer materials must have the ability to permanently "fix " Cr(III) and hence the permanence of fixation must be evaluated for Cr(III)[21]. Bartlett et. al.[3], states "the marvel of the chromium cycle in soil is that oxidation and reduction can take place at the same time." This is an important principle for the application of in situ technologies for the treatment(reduction) of Cr(VI) and permanent fixation of Cr(III).

There is often a certain fraction of Chromium that is so strongly bound that it will either not desorb under ordinary conditions or will desorb at such low rates as to constitute no environmental threat. It is therefore very much essential to estimate the amount of Cr III that can be irreversibly sequestered by a particular soil or sediment. In the case of chromium, it is critical to have an understanding of the Chromium Cycle in the environment. Changes in a contaminant's concentration, pH, redox potential, oxidation state, rate of processes sorp-

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tion and desorption, cation exchange capacity (CEC), clay content, soil solution ratio and carbon content may reduce a contaminant's stability at a site and release it into the environment[4]. Little is known about the release rates of these metals from soils.

Numerous studies of heavy metals in subsurface transport have suggested that sorption and desorption exhibit hysteresis i.e., the two processes are not reversible[14,29,16]. In the past, many attempts have been made to study adsorption of metals on clay mineral surfaces employing macroscopic, kinetic (short-term) or equilibrium approaches[15,24,25,18].

But the dynamic changes in contaminant concentrations caused by chemical reactions such as desorption or dissolution has not been taken into account. It is yet to find theory that is generally applicable for forecasting the occurrence or extent of sorption-desorption hysteresis. The affinity of chemical species for natural sorbents has often been observed to increase from the forward(sorption) to reverse(desorption) direction. The corresponding isotherms are said to manifest non-singularity or hysteresis or different kinetic rates for sorption and desorption(e.g. slower rates and longer time scales for desorption processes). Some degree of hysteresis, or irreversibility, has been observed to occur in the sorption and desorption of contaminants by many soils and sediments[9,8,5].

Hysteresis is the failure of a particular effect to retrace itself when the forces acting to cause sorption are reversed-in other words, a condition for which the effect is not reversible[11,20]. Determining the existence and demonstrating the irreversibility of these mechanisms are key components of a sufficiently protective monitored natural attenuation remedy[34].

For example, the distribution of a contaminant between the aqueous and solid phases after its sorption from solution to the solid is different than after its subsequent release from that solid back into solution. Such differences are also often observed to increase as a function of the period of time that a contaminant remains sorbed to the soil or sediment.

Three key factors must be addressed in considering the potential use of natural attenuation of Cr(Vl) in the subsurface. (i) the reduction capacity of the aquifer (ii) the rate of reduction. (iii) oxidation of Cr(III) to the more toxic hexavalent form. While contamination is actively entering the subsurface, conditions may favor the reduction of Cr (Vl) to Cr(III) thereby immobilizing it in the aquifer soil matrix. After the source of the active contamination is removed, however, chemical parameters within the aquifer, particularly pH, may be altered[22,7,32]. Under the new conditions, which may also favour the desorption of Cr(III) and requires an evaluation of the potential risk of chromium entering the groundwater flow system

Further research is needed to identify conditions where it is most likely to occur more specifically, the rate processes associated with a phenomenon referred to adsorption/desorption hysteresis. Any discussion of sorption desorption of chromium in the subsurface must focus on the soil matrix. Determination of the sorption and desorption behavior of these individual soil components in isolation is a necessary first step towards very detailed understanding and prediction of the hysteresis behaviour of soils of arbitrary composition[13]. It also provides a basis for incorporating hysteresis into equilibrium expressions in Chromium transport and fate models.

Griffin et al.[17] studied the effect of pH on the adsorption of Cr(VI) by the clay minerals kaolinite and montmorillonite, and found adsorption was highly pH dependent; the adsorption of Cr(VI) decreased as pH increased, and the predominant Cr(VI) species adsorbed was $HCrO_4^-$.

In order to analyse and quantify effect of sorption and desorption hysteresis phenomena of Cr(III) in Bentonite, one of the commonly found clay minerals, this study aimed at developing a hysteresis index (HI) that allows quantification of the incomplete desorption behavior of Cr(III) with respect to Bentonite. As such, the HI may serve as a component that includes a quantitative assessment of the degree to which occurrence of desorption of chromium may be identified. This could significantly impact the need for setting design standards for contaminated soil remediation in appropriate circumstances.

Several empirical indices for quantifying hysteresis in soils exist and are presented in TABLE 1. These indices can be subdivided intogroups (i) sorbed concentration q(mol kg^{-1}); (ii) the exponent of the Freundlich equation, N; (iii) the slope of the desorption isotherm in relation to the slope of the sorption isotherm or the func-

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TABLE 1: Hysteresis indices (HI) in the literature[20]

Index based on	Equation	Nomenclature	Ref.
1. Sorbed concentration, q	$HI=Max (q_{desorb} - q_{sorb})/q_{sorb}$	q_{sorb}, q_{desorb}, Solid phase concentrations on sorption and desorption branches of isotherms respectively	[19]
2. Freundlich exponent, N	$HI = N^{sorb}/N^{desorb}$	N^{sorb}, N^{desorb}: Freundlich exponents of sorption and desorption branch, respectively	[28,8,30,35]
3. Slope	$HI=f'_{Sorb}(C)-- f'_{desorb}(C)/f'_{Sorb}(C)$	$f'_{sorb}(C)$, $f'_{desorb}(C)$: first derivatives of the functions describing the adsorption and desorption branches of the isotherm,respectively	[5]

TABLE 2 : Geotechnical properties of Bentonite

Geotechnical property	Bentonite
Maximum dry density g/cm^3	1.37
Specific gravity	2.78
Liquid limit %	375
Plastic limit %	105
Shrinkage limit %	7
pH in water %	9.2
CEC (meq/100g)	80-150
Specific surface area[m^2/g]	700-800
Type	2:1
Swelling potential	High
Silt (2 to 74μm) (%)	18
Clay (< 2μm) (%)	82

tions describing the sorption and desorption isotherm branches[19,35,3,20]. The objective is to derive a measure of hysteresis index for chromium based on the following empirical indices.

EXPERIMENTAL

The materials used for the present study are commercially available Sodium Bentonite $Na_{0.33}(Al, Mg)_2 Si_4 O_{10}(OH)_2 \cdot (H_2O)_n$ as adsorbent and Chromium Nitrate (Cr III) as adsorbate. Bentonite is known as "swelling" or "plastic" clay that effectively sorbs and retains relatively high amounts of water. It is formed from the alteration of siliceous, glass-rich volcanic rocks such as tuffs and ash deposits. The geo technical properties of

Bentonite clay used for the present study is presented in TABLE 2

In order to determine the sorption /desorption hysteresis of chromium on bentonite clay soil batch equilibrium tests were conducted.Batch tests provide a quick method of estimating the maximal contaminant retention capacity of any liner material. The method used in this test was based on the work of Griffin et al.[17], ASTM 1987 and as per recommendations of US EPA/ 530-SW-87-006F

The following conditions were undertaken during experiment for evaluation of sorption /desorption hysteresis phenomenon of Cr(III) in Bentonite clay soil.
1. Varying the Cr(III) concentration (5, 10, 15, 20,25 & 30mg/l)
2. Varying clay-contaminant solution ratio (1:70, 1:80,1:90 &1:100)
3. Varying pH (4, 6,8 &10)
4. Inducing desorption by replacing 80% of the supernatant liquid with contaminant-free solution

This test consists of suspending and stirring clay and contaminant solutions. Clay contaminant solutions were placed in 1000cc glass jar with synthetic rubber plugs and motor with shaft and blades provided for continuously stirring the solutions at 250rpm. After agitation the samples withdrawal for every two-hour from the suspension was taken place. The suspension samples are centrifuged in polypropylene tubes for complete phase separation. Flame Atomic Adsorption Spectrophotometer (Chemito) was used to obtain the concentrations of the chromium in the supernatants under the operating parameters wave length 357.9nm for concentrations 2-8ppm and 425.4nm for concentrations 10-20 ppm. The dissolved chromium (trivalent chromium) is converted to hexavalent state by oxidation with potassium permanganate. The time required to reach equilibrium concentration was studied. After agitation the pH of the sample was tested and recorded. Sodium hydroxide or sulphuric acids is used to adjust pH of the sample.The mass of the sorbed contaminant per unit mass of soil (S) is then obtained through the difference between initial concentration (Co) and equilibrium concentration (Ce) following

S = (Co-Ce)V/M

Where V is the contaminant solution volume and M is the dry mass of the soil.

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TABLE 3 : The best estimated parameters for Sorption Isotherms for Soil solution ratio ranging from 1: 60 to 1:100

Sl. no.	SSR	pH	Best estimated parameters for sorption isotherm				
			R^2	Sm mg/kg	Linear model polynomial $f(x) = p_1*x + p_2$	N_1	% of blank
1.	1:60	4	0.978	696	p_1=33.62, p_2=84.01	0.833	0.51
2.		6	0.987	766	p_1=39.77, p_2=83.69.	0.828	0.75
3.		8	0.979	918	p_1=66.82 , p_2=42.35	1.04	0.07
4.		10	0.992	984	p_1= 66.35 , p_2=165	0.609	0.31
5.	1:70	4	0.979	794	p_1=38.9012, p_2=76.01	0.873	0.24
6.		6	0.956	866	p_1=42.14, p_2=146.7	0.695	-0.11
7		8	0.925	750	p_1=48.6, p_2=196.3	0.744	0.45
8		10	0.910	1034	p_1=52.8, p_2=284.7	0.64	1.02
9	1:80	4	0.956	843	p_1=43.18, p_2= 20.44	1.397	-0.67
10		6	0.947	950	p_1= 47.2,p_2= 112.7	0.683	0.54
11		8	0.896	1021	p_1=50.16,p_2=267.6	0.636	0.73
12		10	0.963	1296	p_1=95.63, p_2=294.3	0.518	0.23
13	1:90	4	0.944	844	p_1=45.34, p_2= - 49.1	1.591	-0.25
14		6	0.969	942	p_1= 37.86, p_2=201	0.921	0.00
15		8	0953	1314	p_1=75.99, p_2=193.3	0.809	0.34
16		10	0.908	1429	p_1=82.89, p_2=370.7	0.574	0.23
17	1:100	4	0.933	900	p_1=48.97$_2$=-66.58	1.734	0.72
18		6	0.834	980	p_1=49.78, p_2=78.23	1.116	0.64
19		8	0.991	1240	p_1=60.1, p_2=324.2	0.737	0.38
20		10	0.965	1538	p_1=82.79, p_2=384.6	0.576	-0.09

Note: Sm -Maximum solid phase concentration, p_1, p_2 & R^2 - Best estimated parameters fitting with linear model polynomial, N_1 - Freundlich exponents of sorption isotherms

TABLE 4 : The best-estimated parameters for desorption Isotherms for soil solution ratio ranging from 1: 60 to 1:100

Sl no.	SSR	pH	Best estimated parameters for Desorption isotherm				
			R^2	Sm mg/kg	Linear model polynomial $f(x) = p_1*x + p_2$	N_2	% of blank
1.	1:60	4	0.98	486	p_1= 27.06, p_2= -9.821	1.046	0.51
2.		6	0.984	654	p_1= 37.66, p_2= 64.59	0.844	0.42
3.		8	0.967	749	p_1=58.73, p_2=1.003	1.088	-0.34
4.		10	0.987	881	p_1=61.14, p_2=147.7	0.682	0.04
5.	1:70	4	0.987	575	p_1=31.81, p_2= -1.195	1.0184	0.68
6.		6	0.975	743	p_1=39.73, p_2= 125.8	1.132	0.40
7		8	0.921	855	p_1= 50.27 p_2=164.8	0.806	0.34
8		10	0.912	941.56	p_1=53.91 p_2=261.4	0.606	0.29
9	1:80	4	0.986	686	p_1=37.75, p_2=19.49	0.9568	-0.34
10		6	0.869	814	p_1=46.49, p_2=88.86	0.956	0.65
11		8	0.841	877	p_1=45.2, p_2=256.1	0.764	-0.12
12		10	0.9415	1164	p_1=81.01, p_2=324.4	0.378	0.32
13	1:90	4	0.946	710	p_1=44.37,p_2= 15.28	0.920	0.27
14		6	0.816	802	p_1= 46.99,p_2= 103.5	0.683	0.33
15		8	0.927	1158	p_1=74.36, p_2=152.8	0.656	0.24
16		10	0.924	1311	p_1= 86.78,p_2=306.9	0.413	0.34
17	1:100	4	0.868	840	p_1=51.14,p_2=-23.26	1.586	-0.045
18		6	0.889	870	p_1= 48.35, p_2=104.9	1.019	0.26
19		8	0.725	1028	p_1=50.97,p_2=30.95	0.732	0.31
20		10	0.969	1360	p_1=83.37, p_2=285.7	0.46	0.34

Note: Sm -Maximum solid phase concentration, p_1, p_2 & R^2 - Best estimated parameters fitting with linear model polynomial,N_2- Freundlich exponents of desorption isotherms

Soil solution ratio is defined as the mass of the dry soil divided by the volume of the solution used in the tests. The soil solution ratio can influence the mass loading on the soil solid phase and the magnitude of sorption nonlinearly increases as the amount of sorbent increases. Soil solution ratio of less than 1:60 would result in pastes that could create difficulties in the mixing, separation and analysis of batch contact. Since sorption is a physico chemical process it is important to evaluate the sorption capacity after equilibrium between the solid and liquid phases has been reached. Following the recommendation made by Roy et al.[17] equilibrium is considered to be achieved, when there is not more than a variation of 5% variation in the concentrations of the suspensions over a 24hr period. Equilibration time was achieved in 24 hrs almost in all sorption and desorption experiments.

Blank solutions were used to evaluate the chemical stability of contaminant solutions. They were submitted to a 24hr period of rotation and the stability was calculated using the following coefficient

% of Blank = $(C_{b1} - C_{b2}) \times 100/C_{b1}$

Where C_{b1} and C_{b2} are the initial and final concentrations of blank solutions respectively.

Desorption experiments were performed by replacing the 80% of the supernatant liquid with contaminant free solution. After agitation the samples withdrawal for every one-hour from the suspension was taken place. The procedure was repeated the same as conducted for the sorption experiments and the desorbed concentrations were determined.

Sorption isotherms and parameter estimation

Isotherms were developed for Constant Soil Solution Ratio(CSR). For CSR isotherms the soil solution ratio was held constant while Chromium concentrations were systematically changed. Linear and Freundlich models were used for fitting and parameter estimation and are presented Linear regression analysis was applied and the best fits were selected using Curve Fitting Toolbox (a collection of graphical user interfaces(GUIs) and M-file functions built on the MATLAB® technical computing environment. The data are fitted using parametric models such as linear polynomials and the Goodness of fit is evaluated using graphical techniques. Parametric fitting produces coefficients that describe the data.

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TABLE 5 : Hysteresis indices developed with the first derivatives of the functions describing the sorption and desorption branches of the isotherms

SSR	1:60	1:70	1:80	1:90	1:100
pH4	0.195	0.182	0.125	0.021	-0.044
pH6	0.0528	0.05733	0.0149	-0.241	0.028
pH8	0.1361	-0.0324	0.0214	0.0987	0.1518
pH10	0.0785	-0.0209	0.152	-0.0468	-0.007

TABLE 6 : Hysteresis indices developed with the Freundlich exponents of sorption and desorption branches of the isotherms

SSR	1:60	1:70	1:80	1:90	1:100
pH4	1.256	1.166	0.684	0.578	0.914
pH6	1.019	1.631	1.400	0.741	0.913
pH8	1.047	1.083	1.201	0.811	0.994
pH10	0.989	0.946	0.729	0.719	0.798

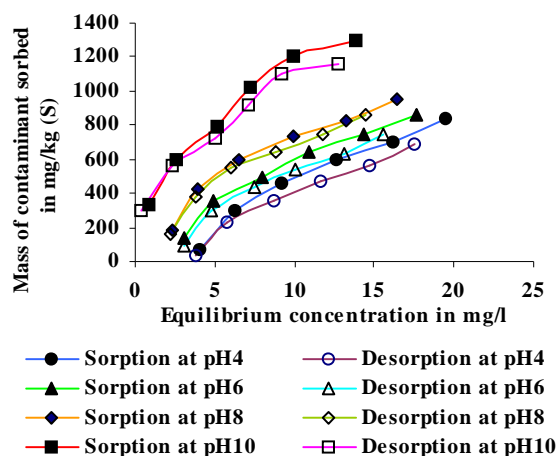**Figure 1: Sorption and desorption isotherms for solid solution ratio 1:60**

Figure 2 : Sorption and desorption isotherms for solid solution ratio 1:70

The Freundlich exponents and the first derivatives of the functions describing the sorption and desorption isotherms are calculated and presented in TABLES 4 and 5.
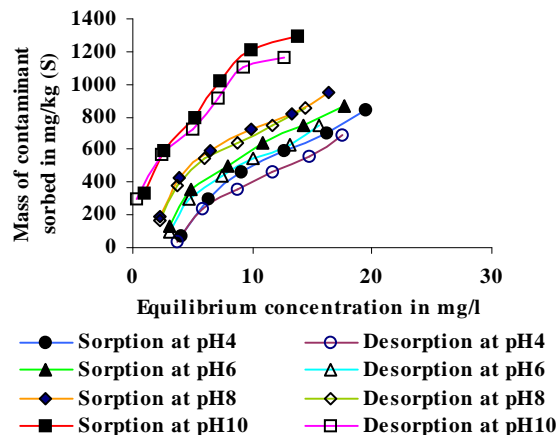

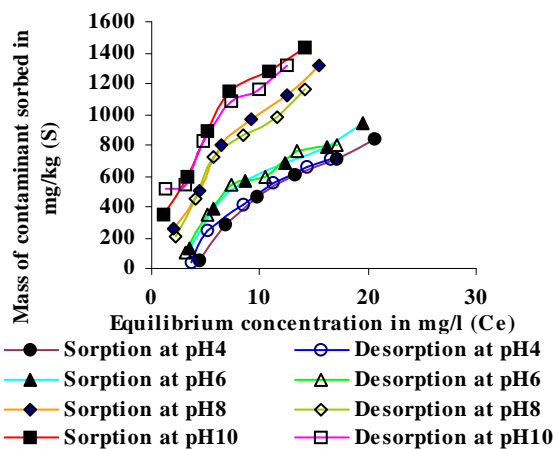**Figure 3 : Sorption and desorption isotherms for solid solution ratio 1:80**

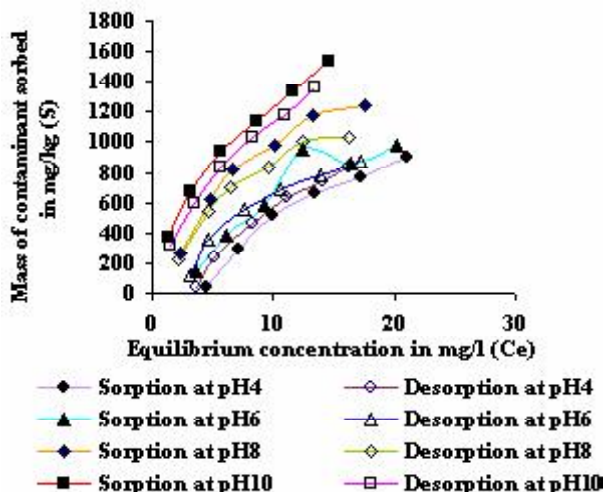**Figure 4 : Sorption and desorption isotherms for 1:90**

Figure 5 : Sorption and desorption isotherms for solid solution ratio 1:100
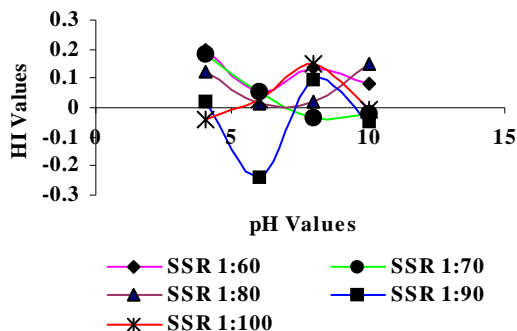
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Figure 6: Variation of HI values (developed on the basis of first derivatives of the functions describing the sorption and desorption branches of the isotherms) with pH and Solid solution ratios with pH & SSR
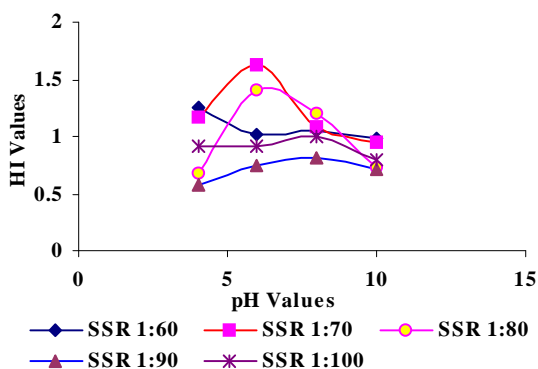

Figure 7: Variation of HI values with pH developed on the basis of Frendulich exponents of sorption and desorption isotherms

RESULTS AND DISCUSSIONS

The hysteresis indices were calculated (as given in TABLE 1) in two ways, one with Freundlich exponents and the other with the first derivatives of the functions describing the sorption and desorption isotherm branches. Both ways expressed a good representation of variation of HI values with pH. Solid solution ratio also has remarkable influence on the sorption and desorption hysteresis effect of Chromium with bentonite

1. It is evident from the results that both pH and Solid solution ratio have remarkable influence and produce Hysteresis effect in the sorption and desorption behavior of Cr III in Bentonite.
2. It is observed that the sorption of Cr III increases with increasing pH in Bentonite.
3. When the HI values increased there exists stronger irreversibility of the contaminant and vice versa.

4. The HI values decrease with increasing pH and Solid solution ratio.
5. From TABLE-4 for the pH 4, when the SSR value increased from 1:60 to 1:100 the HI values gradually decreased and for SSR value 1:100 it is almost negative that indicates the irreversibility does not occur.
6. For pH 6, when the Solid solution ratio increased from 1:60 to 1:80 it is observed that there is no much variation in the HI value. But when the SSR is increased to 1:90 the HI value decreased to large extent. Again when the SSR increased to 1:100 the HI value increased.
7. Little amount of irreversibility exists for pH 8 in SSR values from 1:70,1:80& 1:90.
8. Higher irreversibility is pronounced for lower pH values and vice versa.
9. From TABLE 5 it is observed that for higher Solid solution ratio as observed for 1:100, the effect of pH on is not significant on the variation of Hysteresis index.
10. However the Hysterisis Indices developed suffer the following limitations (a) they depend on a specific isotherm model (b) depend arbitrarily on solid solution ratios (c) applicable only to a single step desorption isotherms. There are possibilities of multi step desorption stages. In spite of the above limitations a molecular level knowledge in the quantification of Hysterisis Index for assessing the occurrence of irreversibility of the contaminant is attained.

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