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### Cadmium Decontamination from Aqueous Media Using Lateritic Minerals

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## SEPARATION SCIENCE AND TECHNOLOGY

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## Cadmium Decontamination from Aqueous Media Using Lateritic Minerals

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### ABSTRACT

In this study, lateritic minerals were exploited to evaluate their potential for the decontamination of cadmium ions from aqueous solutions as well as for understanding the nature of the decontamination mechanism. Various physicochemical parameters, such as selection of appropriate electrolyte, equilibration time, amount of adsorbent, concentration of adsorbate, effect of diverse ions, and temperature, were studied to simulate the best conditions in which this material can be used as an adsorbent. Maximum adsorption was observed at  $0.005 \text{ mol L}^{-1}$  acid solutions ( $\text{HNO}_3$ ,  $\text{HCl}$ , and  $\text{HClO}_4$ ) using  $0.2 \text{ g}$  of adsorbent for  $8.89 \times 10^{-5} \text{ mol L}^{-1}$  cadmium concentration in 10 minutes equilibration time. Studies show that the adsorption of cadmium decreases with the increase in the concentrations of all the acids. The adsorption data follows the Freundlich isotherm over the range of  $1.78 \times 10^{-5}$  to  $1.78 \times 10^{-3} \text{ mol L}^{-1}$  cadmium concentration.

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2004

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The characteristic Freundlich constants, i.e.,  $1/n = 0.61 \pm 0.02$  and  $K = 5.14 \times 10^{-4} \pm 1.14 \times 10^{-5} \text{ mol g}^{-1}$  have been computed for the sorption system. The sorption mean free energy from the Dubinin–Radushkevich isotherm is  $10.1 \pm 0.6 \text{ kJ mol}^{-1}$ , indicating an ion-exchange mechanism of chemisorption. The uptake of cadmium increases with the rise in temperature (278 to 323 K). Thermodynamic quantities, i.e.,  $\Delta G$ ,  $\Delta S$ , and  $\Delta H$  were also been calculated for the system. The sorption process was found to be exothermic.

**Key Words:** Cadmium; Decontamination; Adsorption; Lateritic minerals.

## INTRODUCTION

Contamination of surface waters by heavy metals due to industrial and human activities is becoming a serious issue in recent years. Cadmium is toxic to human beings due to its very long biologic half life and can cause physiologic disorders even at a very low concentration. The harmful effects of cadmium have been well documented in the literature.<sup>[1–2]</sup> Significant amounts of cadmium enter into aquatic system through nonferrous mining and smelting, incineration of municipal waste containing plastic and nickel–cadmium batteries, phosphate fertilizers, effluents from industries of cadmium bearing alloys, soldering materials, Cd–Ni batteries, and nuclear reactors, where cadmium is used to control the fission as reactor poison. Occupational exposure also takes place in the metal-plating, pigment, and plastic industries. All of these sources contribute to making water toxic beyond 0.01 mg of Cd L<sup>-1</sup>, the permissible limit for human consumption. Keeping in view the gravity of the situation, global attention has been diverted toward understanding the behavior of cadmium in the ecosystem and metabolism for adopting measures for its efficient removal from industrial and municipal waste effluents before their safe disposal into water bodies.

Removal/preconcentration of cadmium from aqueous media has been achieved by different procedures, such as reductive precipitation,<sup>[3,4]</sup> solvent extraction,<sup>[5,6]</sup> ion exchangers,<sup>[7,8]</sup> and adsorption. The adsorbents used for cadmium include activated carbon,<sup>[9]</sup> bentonite,<sup>[10]</sup> soil,<sup>[11,12]</sup> zeolite,<sup>[13]</sup> chelating resin,<sup>[14,15]</sup> and metal oxides.<sup>[16–19]</sup> All of these methods are effective for the removal of cadmium from the waste or polluted waters but are either time consuming or expensive, hence, there is a need to look into other inexpensive and effective methods for this purpose.

The inorganic oxides and hydroxides are preferred adsorbents of metal ions due to their superior sorption characteristics and high resistance to heat

**Cadmium Decontamination****2005**

and radiation. The objective of the present study was to optimize the best conditions for the adsorption of cadmium on naturally available lateritic minerals (LM) from aqueous solution. LM was selected since it is abundantly available at very low cost and the main constituents of the weathering product are goethite, hematite, magnetite, alumina, and quartz, all of which are good adsorbents.<sup>[20–22]</sup> It is also the continuation of our previously studied naturally occurring material used for the decontamination of chromium, silver, and lead from industrial effluents.<sup>[23–25]</sup>

**EXPERIMENTAL PROCEDURE****Preparation of Radiotracer**

The radiotracer of cadmium  $^{115m}\text{Cd}$  ( $t_{1/2} = 44.8\text{d}$ ) used in the present work was prepared by irradiating a known weight of spec-pure cadmium oxide (Johnson and Mathey) in a 10 MW swimming pool type research reactor (PARR-1) of this institute for an appropriate time at a neutron flux density of  $4.5 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ . After a suitable cooling time, the irradiated oxide was dissolved in a minimum amount of distilled nitric acid, heated to near dryness, and the residue was dissolved in 0.2 M nitric acid solution and kept as a stock solution for further use.

**Reagents**

Buffer solutions of pH 1 to 10, having ionic strength of  $0.1 \text{ mol L}^{-1}$ , were prepared by using appropriate volumes of solutions of KCl and HCl (pH 1 to 3),  $\text{CH}_3\text{COONa}$  and  $\text{CH}_3\text{COOH}$  (pH 4 to 6),  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  (pH 6 to 7.5), and  $\text{H}_3\text{BO}_3$ , NaCl and NaOH (pH 8 to 10). All pH measurements were made with a Metrohm 605 digital pH meter equipped with a combined glass/calomel electrode. All the reagents used were of analytical grade and used as such. Distilled and deionized water was used throughout.

The lateritic minerals (LM) used in the present study were obtained from local deposits. The material collected from various sites was ground to a particle size of 100 mesh and shaken in a vibrating mill to minimize the associated heterogeneity. This material was then used without any further physical or chemical pretreatment to simulate natural conditions as far as possible.



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### Sorption Measurements

A known amount of lateritic minerals was taken in a 35 cm<sup>3</sup> screw-top culture tube along with 5 cm<sup>3</sup> of standard acid or buffer solution of known pH. A fixed amount of stock radiotracer solution was also added. Subsequently, the contents were equilibrated on a mechanical shaker for a specific time, centrifuged at 5000 rpm for phase separation, and a supernatant solution was withdrawn. The radioactivity of solutions before (A<sub>i</sub>) and after (A<sub>f</sub>) equilibrium were measured with a NaI well-type scintillation counter (Canberra) coupled with a counter-scaler (Nuclear Chicago). A volume of 1.0 mL was usually used to measure the count rate. All experiments were conducted at ambient temperature (296 ± 1 K) unless otherwise specified.

## TREATMENT OF DATA

### Adsorption of Metal

The percentage adsorption of metal ion, M, from the solution was calculated using the following relationship:

$$\% \text{adsorption} = \frac{A_i - A_f}{A_i} \quad (1)$$

The distribution coefficient (K<sub>d</sub>) was calculated from the equation

$$K_d = \frac{A_i - A_f}{A_f} \times \frac{V}{m} \quad (2)$$

where

A<sub>i</sub> = initial concentration of metal in the solution (mol L<sup>-1</sup>)

A<sub>f</sub> = concentration of metal in solution after equilibrium (mol L<sup>-1</sup>)

V = volume of adsorbate solution (cm<sup>3</sup>)

m = amount of adsorbent (g)

### Calculation of Thermodynamic Parameters

Thermodynamic parameters were calculated using the following relations:

$$K_c = \frac{C_{\text{ads}}}{C_{\text{eq}}} \quad (3)$$

where

K<sub>c</sub> = equilibrium constant

C<sub>ads</sub> = equilibrium concentration of metal on the adsorbent (mol L<sup>-1</sup>)

**Cadmium Decontamination****2007**

$C_{eq}$  = equilibrium concentration of metal in solution (mol L<sup>-1</sup>)  
If  $F_0$  is the fractional attainment of adsorption at equilibrium, then

$$C_{eq} = C_i(1 - F_e) \quad (4)$$

and

$$C_{ads} = C_i F_e \quad (5)$$

where

$C_i$  = initial concentration of metal in solution

$F_e$  = fractional attainment of metal concentration at equilibrium

By substituting the values of  $C_{eq}$  and  $C_{ads}$  from Eqs. (4) and (5) into Eq. (3),  $K_c$  becomes:

$$K_c = \frac{F_e}{(1 - F_e)} \quad (6)$$

which shows that the equilibrium constant is independent of the amount of adsorbent and of the volume of the solution.

The values of  $\Delta H$  and  $\Delta S$  were calculated from the slope and intercept of the linear van't Hoff plot, respectively, using the relation:

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (7)$$

where

$\Delta S$  = entropy change for the process

$\Delta H$  = enthalpy change for the process

$R$  = gas constant

$T$  = absolute temperature

The changes in standard free energy ( $\Delta G$ ) and entropy ( $\Delta S$ ) for the specific adsorption were also calculated using the equations:

$$\Delta G = -RT \ln K_c \quad (8)$$

$$\Delta G = \Delta H - T \Delta S \quad (9)$$

$$\Delta S = (\Delta H - \Delta G)/T \quad (10)$$

where the symbols have their usual significance.



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## RESULTS AND DISCUSSION

The adsorption of cadmium ions from aqueous solutions on lateritic minerals was examined by optimizing specified physicochemical parameters, such as variable concentrations of mineral acids, pH, equilibration time, amount of adsorbent and concentration of adsorbate, using batch method, and radiotracer technique. The effect of temperature on the adsorption of cadmium was also checked. The criterion for the optimization was the selection of parameters where maximum adsorption occurred. All the reported results are the average of at least triplicate independent measurements. The determined relative standard deviation was within  $\pm 3.0\%$  unless otherwise specified.

### Characterization of Adsorbent

The main mineral constituents of the LM used were determined employing optical microscopy and x-ray diffraction.<sup>[26]</sup> The determined mineralogical constituents are reported in Table 1, which revealed that the LM is mainly composed of hydrous oxides of iron-bearing minerals. The chemical composition of the LM was characterized by using instrumental neutron activation analysis (INAA)<sup>[27,28]</sup> and the results are shown in Table 2.

**Table 1.** Mineral constituents of the lateritic minerals.

Constituent	Formula
Goethite	FeOOH
Hematite	Fe <sub>2</sub> O <sub>3</sub>
Limonite	2Fe <sub>2</sub> O <sub>3</sub> .3H <sub>2</sub> O
Magnetite	Fe <sub>3</sub> O <sub>4</sub>
Quartz	SiO <sub>2</sub>
Diaspore	AlOOH
Enstatite/saprolite	Mg <sub>2</sub> (Si <sub>2</sub> O <sub>6</sub> )
Ilmenite	FeTiO <sub>3</sub>
Olivine	MgFeSiO <sub>4</sub>
Dolomite	Ca-MgCO <sub>3</sub>
Bauxite	Al <sub>2</sub> O <sub>3</sub> .2H <sub>2</sub> O

**Cadmium Decontamination****2009**

**Table 2.** Chemical composition of lateritic minerals.

Element	Concentration %
Fe	34.0–41.0
Mg	3.80–6.33
Al	4.8–9.3
Si	8.63–13.60
Zn	0.01–0.08
Ca	4.23–16.4
Mn	0.51–0.83
Ni	0.31–0.55
Cu	0.07–0.09
Cr	0.35–0.52
Co	0.05–0.08
Ti	0.83–1.89

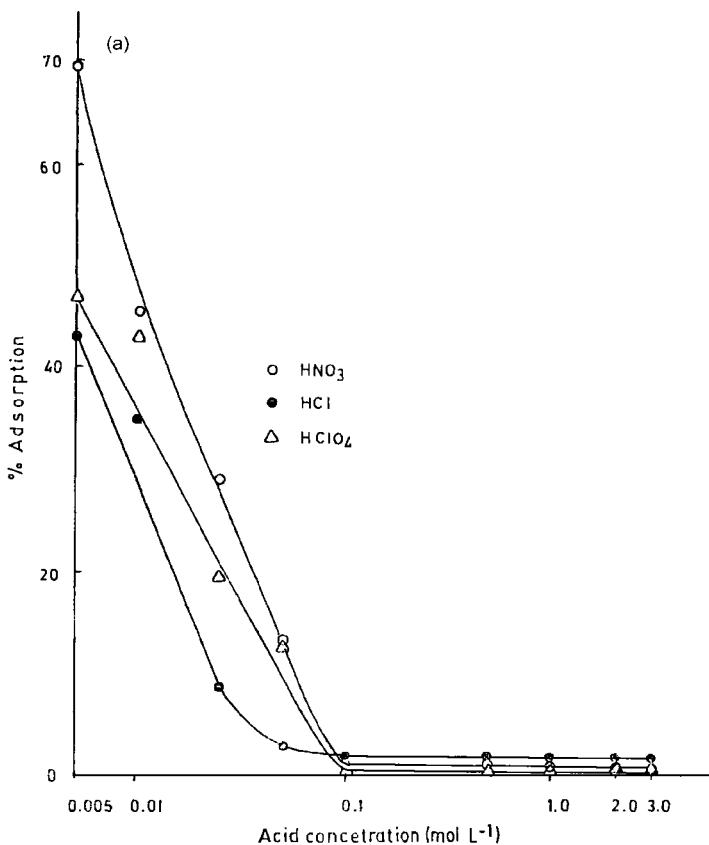
**Effect of Acid Concentration**

Interaction of various chemical compounds and electrolytes with oxides may alter the surface properties, therefore, adsorption behavior of cadmium ( $8.89 \times 10^{-5}$  mol L<sup>-1</sup>) was investigated in mineral acid solutions of nitric, hydrochloric, and perchloric acid having a concentration range from 0.005 to 3.0 M using 0.2 g of LM. The results presented in Fig. 1 show that maximum adsorption of cadmium ions was observed at 0.005 M acid concentration, which then decreases with an increase in acid concentration from 0.005 to 3.0 M. Similar trends have been observed for the adsorption of silver and lead on mineral mixture.<sup>[24,25]</sup> The decrease in adsorption of cadmium with an increase in acid concentration may be attributed to the competition between the excess of H<sup>+</sup> ions in the medium and positively charged hydrolyzed species present in the solution. Also, a higher acid concentration appears to suppress hydrolysis of the element in hydrolyzed species, resulting in lower adsorption. It was also observed that maximum adsorption of cadmium occurred in 0.005 M HNO<sub>3</sub> as compared to the other acids, therefore, this concentration of HNO<sub>3</sub> was used for all the subsequent experiments regarding the optimization of conditions for the adsorption of cadmium on LM.

The adsorption of metal ions on hydrous metal oxide surface can probably be explained on the basis of the surface complex formation model. In this

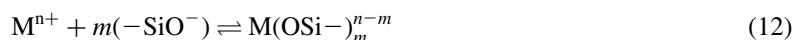
2010

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**Figure 1.** (a) Variation of percent adsorption of cadmium on lateritic minerals as a function of acid concentration. (b) Variation of  $K_d$  for the adsorption of cadmium on lateritic minerals as a function of acid concentration.

model, the hydrolysis of silicon dioxide, which is the second major constituent of LM, produces hydrous oxide surface group  $-\text{SiOH}$  i.e., the silanol group. This results in the formation of silica a surface as weakly acidic with  $K_a = 10^{-6}$  to  $10^{-8}$ .<sup>[29]</sup> The cation exchange reaction can occur in aqueous solutions as follows:



## Cadmium Decontamination

2011

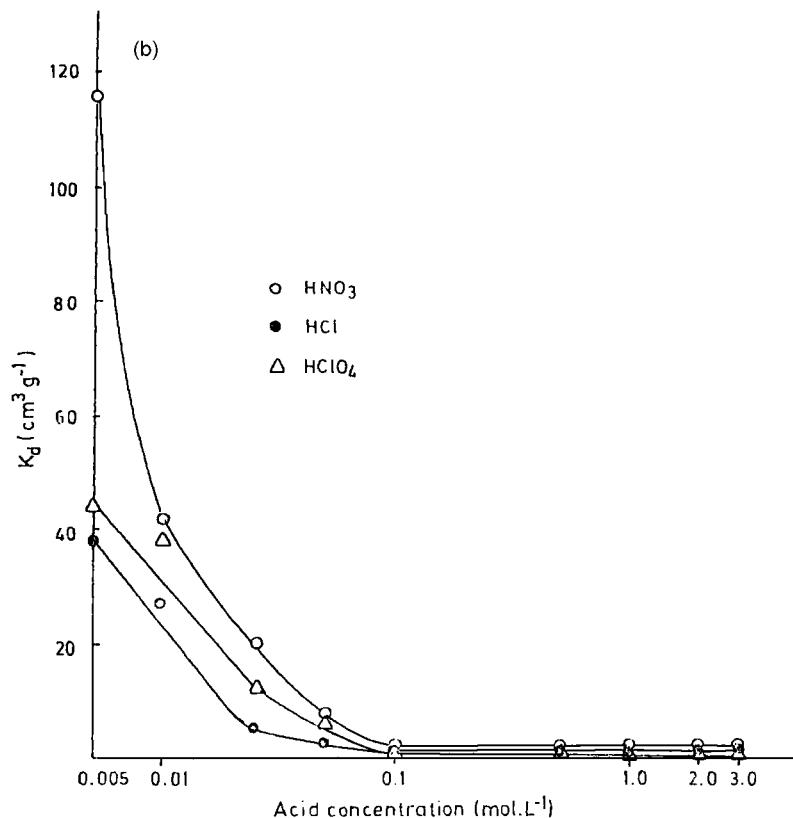
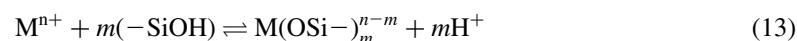


Figure 1. Continued.

The overall reaction can be represented as:



where

$\text{M}^{n+}$  = metal ion with  $n^+$  charge

$-\text{SiOH}$  = silanol group on  $\text{SiO}_2$  surface

$m \text{ H}^+$  = number of protons released

Reaction<sup>[13]</sup> is reversible in acid solution. In the present study, the decrease in the adsorption of cadmium at higher acid concentration can be explained on the basis of competitive reaction of the protons in the medium and positively charged cadmium ions. The maximum adsorption of metal at



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0.005 M acid concentration is in accordance with the concept of zero point charge (ZPC) of  $\text{SiO}_2$ , which lies in the range of  $2.0 \pm 0.2$ .<sup>[30]</sup> This indicates that the adsorption of metal occurs on the surface of  $\text{SiO}_2$  present in LM.

### Variation of pH

The removal of cadmium from aqueous solutions by adsorption is highly dependent on the pH of the solution, which affects the surface charge of the adsorbent, degree of ionization, and speciation of the adsorbate species. Such study helps in indicating the appropriate pH of the effluent/waste water for achieving maximum efficiency in the removal of metal ions by an adsorbent. The pH dependence study of cadmium adsorption ( $8.89 \times 10^{-5} \text{ mol L}^{-1}$ ) on LM was, therefore, carried out using 10 mL of buffer solutions of different pH covering a range of 1 to 10, using 0.2 g of adsorbent. The results obtained are shown in Fig. 2. The percent adsorption gradually increases up to pH 5. With further increases in pH of the solution, the adsorption was rapidly increased and was quantitative at pH 6 and above. Similar trends are reported for the adsorption of europium on mineral mixture.<sup>[31]</sup>

The lower adsorption of cadmium from pH 1 to 4 can be attributed to the presence of oxide and hydroxide of iron as major constituents of LM, which possess a positively charged surface below pH 6 and negatively charged sites above the isoelectric point of 5.4 to 9.0.<sup>[30]</sup> The enhanced adsorption of cadmium ions at 6.0 pH could probably be due to the condensation reaction between the hydrolysis products of the sorbate ions and the sorbent carrying -OH groups.<sup>[32]</sup> It can, therefore, be concluded that the overall adsorption of cadmium ions on the surface of the LM used is mainly due to the combined effect of hydrous oxides of iron and silica present in the LM.

### Influence of Equilibration Time

The time-dependence adsorption of cadmium on LM was studied using 10.0  $\text{cm}^3$  of  $8.89 \times 10^{-5} \text{ mol L}^{-1}$  of cadmium solution in 0.005 mol  $\text{L}^{-1}$  of  $\text{HNO}_3$  with 0.2 g of lateritic minerals. The equilibration time was varied from 0.5 to 15 minutes and results are shown in Fig. 3. It is seen that the percentage adsorption increases with the increase in equilibration time. Maximum adsorption was observed at 10 minutes time, beyond which there is no further increase in the adsorption. Therefore, 10 minutes equilibration time was considered sufficient for the adsorption of cadmium on lateritic minerals and

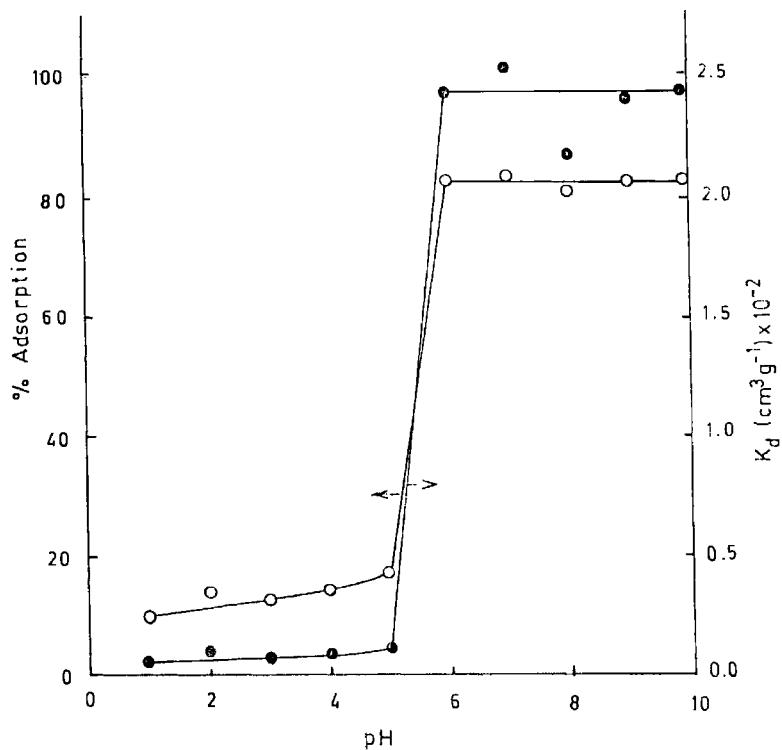


Figure 2. Effect of pH on the adsorption of cadmium on lateritic minerals.

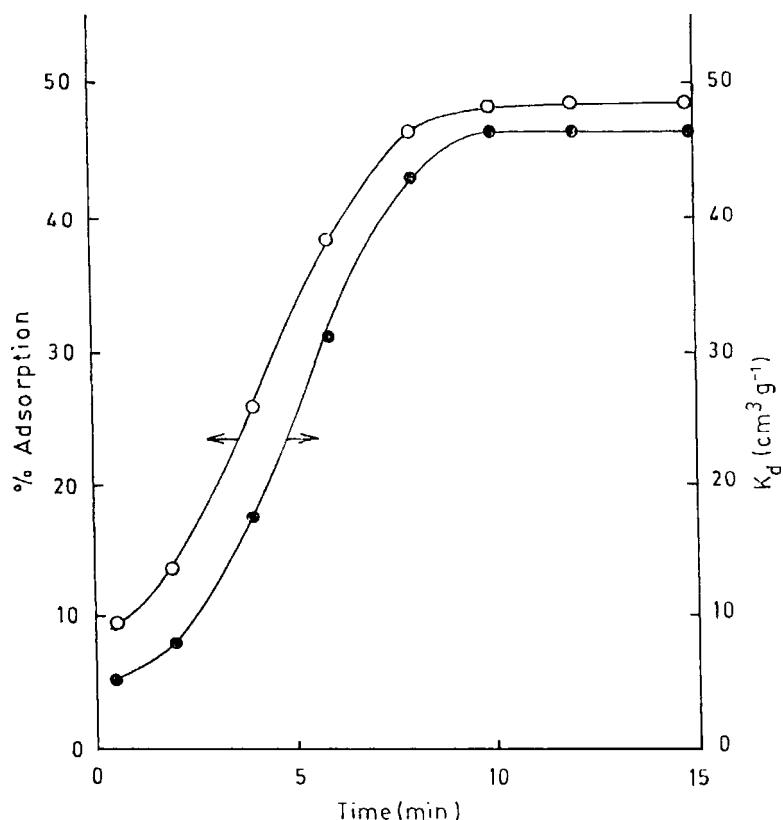
was employed for all the subsequent experiments. The short equilibration time suggests that the adsorption process is a surface phenomenon.<sup>[33]</sup>

#### Effect of Amount of Adsorbent

The influence of the amount of adsorbent on the adsorption efficiency was also studied by shaking 10 cm<sup>3</sup> of  $8.89 \times 10^{-5}$  mol L<sup>-1</sup> of cadmium solution using the optimized parameters. The amount of lateritic minerals was varied from 0.05 to 1.4 g and the results are represented in Fig. 4, which depicts that 1.0 g of lateritic minerals is sufficient for the quantitative removal of cadmium from the aqueous solution used. This amount of lateritic minerals was used for further investigations.

2014

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**Figure 3.** Influence of equilibration time on the adsorption of cadmium on lateritic minerals.

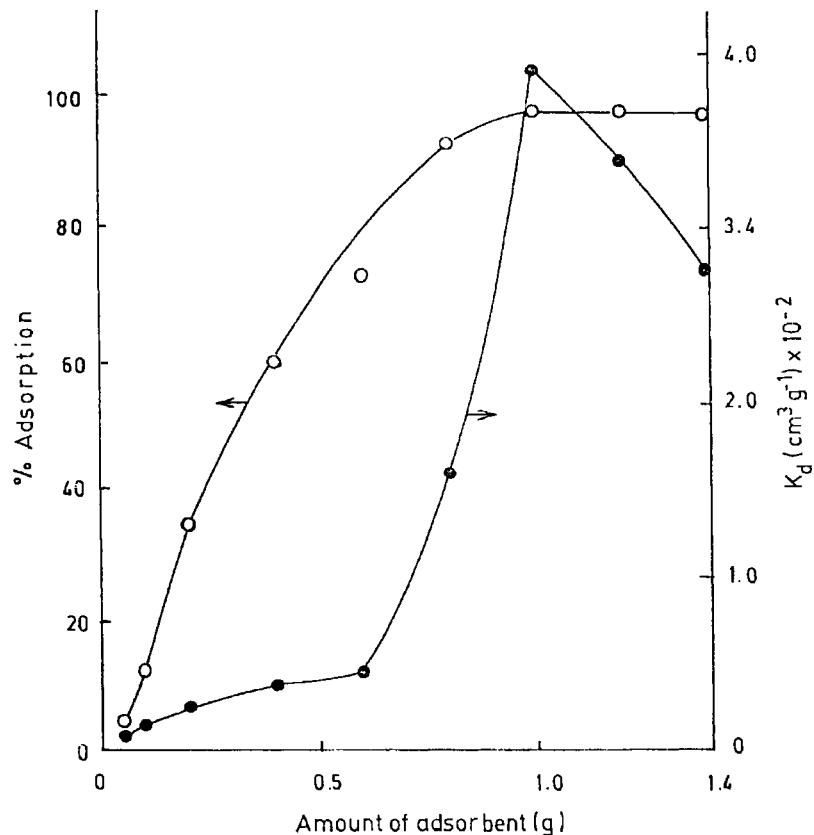
#### Variation of Adsorbate Concentration

Concentration dependence of cadmium adsorption on lateritic minerals was studied under the optimized conditions of acid concentration, equilibration time, and the amount of adsorbent. The initial sorptive concentration of cadmium was varied from  $1.78 \times 10^{-5}$  to  $1.78 \times 10^{-3}$  mol L<sup>-1</sup>. It was observed that the adsorption of cadmium decreased with the increase in initial concentration. This can be explained in terms of relatively lesser number of active sites at higher concentrations of cadmium.

The results of the cadmium adsorption on lateritic minerals at various concentrations ( $10^{-5}$  to  $10^{-3}$  mol L<sup>-1</sup>) were analyzed in terms

## Cadmium Decontamination

2015



**Figure 4.** Effect of amount of adsorbent on the adsorption of cadmium on lateritic minerals.

of the Freundlich mode of adsorption. It was found that the Freundlich adsorption isotherm was capable of describing the data over the entire range of concentration studied. The Freundlich model is expressed as

$$C_{\text{ads}} = K C_{\text{eq}}^{1/n} \quad (14)$$

The linearized form of the Freundlich isotherm is:

$$\log C_{\text{ads}} = \log K + 1/n \log C_{\text{eq}} \quad (15)$$

where

$C_{\text{ads}}$  = amount of cadmium adsorbed on LM at equilibrium ( $\text{mol g}^{-1}$ )

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$C_{eq}$  = equilibrium concentration of cadmium in solution (mol L<sup>-1</sup>)  
K and 1/n = Characteristic constants

A plot of  $\log C_{ads}$  vs.  $\log C_{eq}$  yields a straight line (Fig. 5). This linear plot supports the applicability of the Freundlich isotherm model in the present study. The numerical values of adsorption capacity (K) and intensity (1/n) were evaluated from the intercept and slope of the straight line, using a least-square fit program, and were found to be  $5.14 \times 10^{-4} \pm 1.14 \times 10^{-5}$  mol g<sup>-1</sup> and  $0.61 \pm 0.02$ , respectively. The fractional value of 1/n ( $0 < 1/n < 1$ ) precludes the heterogeneous surface of the lateritic minerals.<sup>[34]</sup> The applicability of Freundlich isotherm in the present system is similar to earlier adsorption studies of silver and lead on mineral mixture.<sup>[24,25]</sup>

To classify the physical or chemical adsorption, the data were applied to Dubinin–Radushkevich (D–R) isotherm model. The D–R equation is:

$$C_{ads} = C_m \exp(-B\epsilon^2) \quad (16)$$

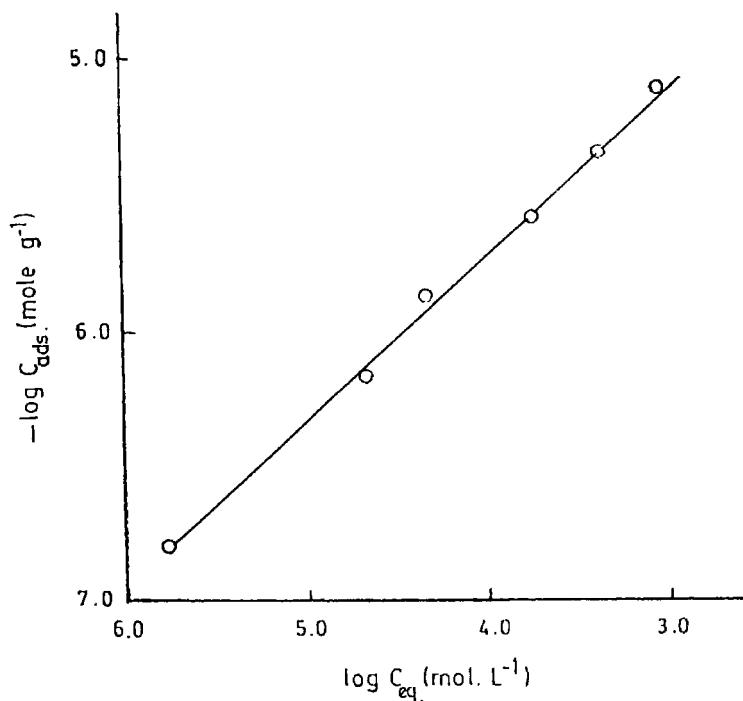


Figure 5. Freundlich adsorption isotherm of cadmium on lateritic minerals.

## Cadmium Decontamination

2017

Where  $C_{ads}$  is the amount of cadmium adsorbed on LM,  $C_m$  is the maximum amount of cadmium that can be adsorbed on LM under the optimized experimental conditions, B is a constant with a dimension of energy, and  $\epsilon \in$  (Polyanyi potential) =  $RT\ln(1 + 1/C_{eq})$ , where R is the gas constant in  $\text{kJ mol}^{-1} \text{ K}^{-1}$ , T is the absolute temperature in K, and  $C_{eq}$  is the equilibrium concentration of cadmium in solution. The linearized form of D-R isotherm is

$$\ln C_{ads} = \ln C_m - B\epsilon^2 \quad (17)$$

When  $\ln C_{ads}$  was plotted against  $\epsilon^2$ , a straight line was observed (Fig. 6). The computed values of B and  $C_m$  from the slope and intercept of this straight line were  $-4.95 \times 10^{-3} \pm 2.9 \times 10^{-4} \text{ kJ}^2 \text{ mol}^{-2}$  and  $2.67 \times 10^{-5} \pm 4.64 \times 10^{-7} \text{ mol g}^{-1}$ , respectively. From the calculated value of B, the mean

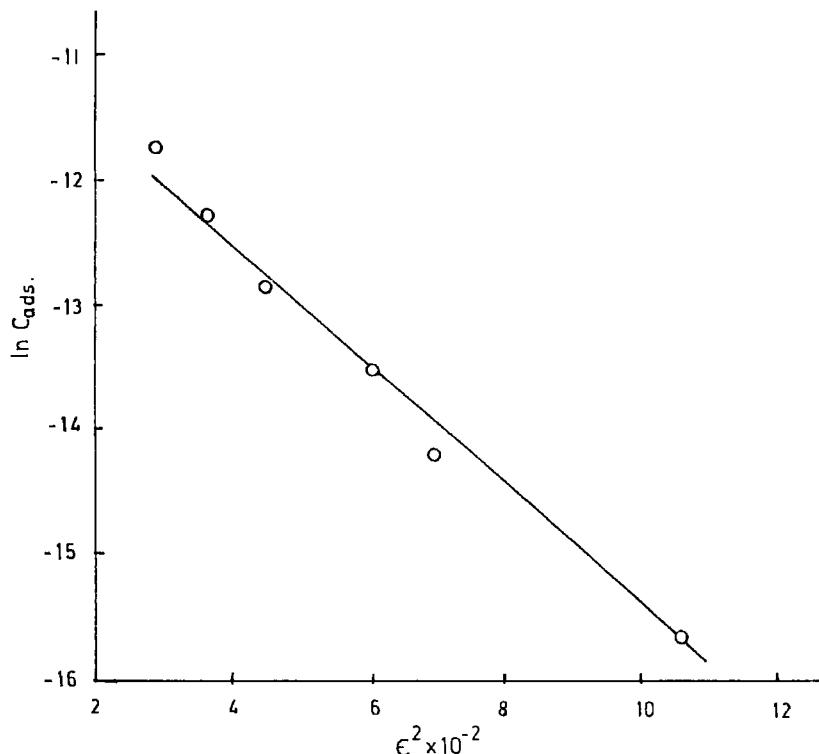


Figure 6. Dubinin-Radushkevich adsorption isotherm of cadmium on lateritic minerals.



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sorption energy (E) was computed as:

$$E = \frac{1}{\sqrt{-2B}} \quad (18)$$

which is the free energy of transfer of 1 mol of solute from infinity to the surface of LM. The numerical value of E evaluated from Eq. (18) is  $10.1 \pm 0.6 \text{ kJ mol}^{-1}$ , which is in the expected range of 8 to  $16 \text{ kJ mol}^{-1}$  for chemisorption based on ion exchange phenomena.<sup>[35,36]</sup>

### Effect of Diverse Ions

The presence of other cations and anions in the adsorptive medium may change the environment and solution chemistry of the metal of interest, which effects the adsorption efficiency of an adsorbent. Therefore, using the optimized parameters, the adsorption of cadmium ions ( $8.89 \times 10^{-5} \text{ mol L}^{-1}$ ) on lateritic minerals was also studied in the presence of high concentrations of various cations and anions are commonly found in samples of ground water. The results are shown in Table 3. All the anions were used as their sodium salts; whereas for cations, the nitrate salts were used. The perusal of the data in

**Table 3.** Effect of diverse ions on the adsorption of cadmium ions on lateritic minerals.

Ions	Compound used	Concentration $\times 10^3$ (mol L $^{-1}$ )	Adsorption (%)
None	—	—	99.62
Nitrate	NaNO <sub>3</sub>	5.00	99.45
Chloride	NaCl	5.00	99.16
Perchlorate	NaClO <sub>4</sub>	5.02	97.58
Sulphate	Na <sub>2</sub> SO <sub>4</sub>	5.01	97.62
Acetate	NaCH <sub>3</sub> COO	5.08	96.65
Carbonate	Na <sub>2</sub> CO <sub>3</sub>	0.42	97.25
Bicarbonate	NaHCO <sub>3</sub>	0.49	97.73
Sodium	NaNO <sub>3</sub>	26.10	95.78
Potassium	KNO <sub>3</sub>	7.67	96.30
Calcium	Ca(NO <sub>3</sub> ) <sub>2</sub>	7.48	85.67
Magnesium	Mg(NO <sub>3</sub> ) <sub>2</sub>	12.34	89.96
Zinc	Zn(NO <sub>3</sub> ) <sub>2</sub>	0.76	96.42
Iron	Fe(NO <sub>3</sub> ) <sub>3</sub>	0.45	98.57



Table 3 shows that the adsorption of cadmium on lateritic minerals was almost quantitative in the presence of all the ions studied except calcium and magnesium, which decreased the adsorption by 14% and 10%, respectively. This decrease in the adsorption of cadmium is probably due to the utilization of the adsorption sites on the surface of lateritic minerals by these ions.

### Effect of Temperature

The effect of temperature on the adsorption of cadmium ions ( $8.89 \times 10^{-5}$  mol L<sup>-1</sup>) on lateritic minerals was also checked using the optimized conditions. The temperature was varied from 278 to 323 K. The amounts of cadmium ion adsorbed at various temperatures are shown in Table 4, which reveals that the uptake of cadmium increases with the rise in temperature, indicating better adsorption at higher temperature. Similar results have also been reported for the adsorption of silver<sup>[24]</sup> and lead<sup>[25]</sup> on mineral mixture. The enhanced amount of cadmium adsorbed at equilibrium with the rise in temperature may be either due to acceleration of some originally slow adsorption steps or due to the creation of some new active sites on the adsorbent surface.

The amounts of cadmium adsorbed at equilibrium at different temperatures have been utilized to evaluate the thermodynamical parameters for the sorption system. The van't Hoff plot of  $\ln K_c$  vs  $1/T$  was a straight line (Fig. 7). The values of  $\Delta H$  and  $\Delta S$  can be calculated from the slope (- $\Delta H/R$ )

**Table 4.** Adsorption studies of cadmium ions on lateritic minerals as a function of temperature.

Temperature (k)	1/t (K <sup>-1</sup> )	Concentration adsorbed (mol l <sup>-1</sup> )	Concentration in bulk (mol l <sup>-1</sup> )	K <sub>c</sub>	In K <sub>c</sub>
278	$3.597 \times 10^{-3}$	$7.819 \times 10^{-5}$	$1.076 \times 10^{-5}$	7.27	1.98
296	$3.378 \times 10^{-3}$	$8.255 \times 10^{-5}$	$6.405 \times 10^{-6}$	12.89	2.56
308	$3.247 \times 10^{-3}$	$8.471 \times 10^{-5}$	$4.252 \times 10^{-6}$	19.92	2.99
323	$3.096 \times 10^{-3}$	$8.585 \times 10^{-5}$	$3.114 \times 10^{-6}$	27.57	3.32

lateritic minerals = 1000 mg,  
shaking time = 10.0 min,  
volume equilibrated = 10 cm<sup>3</sup>,  
concentration of HNO<sub>3</sub> = 0.005 mol L<sup>-1</sup>, and  
concentration of cadmium =  $8.89 \times 10^{-5}$  mol L<sup>-1</sup>.

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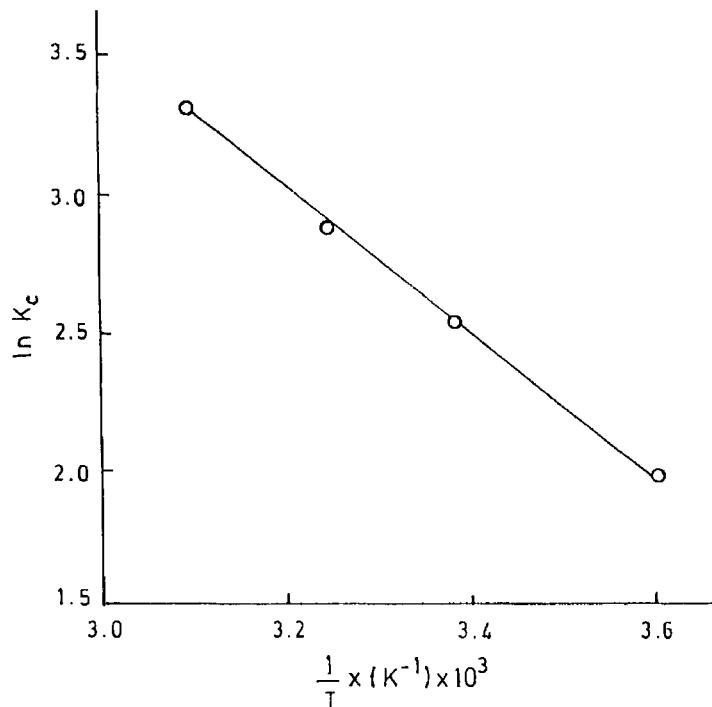


Figure 7. Van't Hoff plot for the adsorption of cadmium on lateritic minerals.

and intercept ( $\Delta S/R$ ) of this straight line. By using the Eq. (7), the estimated  $\Delta H$  value for the present system was  $-22.56 \text{ kJ mol}^{-1}$  (Table 5). The values of free energy of specific adsorption,  $\Delta G$ , and entropy  $\Delta S$  at various temperatures were calculated by using Eqs. (8) and (9) and are listed in

Table 5. Thermodynamic parameters for adsorption of cadmium ions on lateritic minerals.

Temperature (K)	$\Delta G$ (kJ. mol $^{-1}$ )	$\Delta H$ (kJ. mol $^{-1}$ )	$\Delta S$ (JK $^{-1}$ . mol $^{-1}$ )
278	-4.58		-64.66
296	-6.29	-22.56	-54.96
308	-7.66		-48.37
323	-8.91		-42.26



Table 5. The negative values of  $\Delta G$  indicate the spontaneity of the uptake process of cadmium on lateritic minerals. The increase in the numerical value of  $-\Delta G$  with the rise in temperature indicates that the sorption process of cadmium ions on lateritic minerals becomes more favorable at higher temperatures. The negative value of enthalpy change ( $\Delta H$ ) confirms the exothermic chemisorption process of cadmium adsorption on lateritic minerals. The negative value of  $\Delta S$  suggests the decrease in randomness at the solid–solution interface by the fixation of cadmium ions on the active sites of the adsorbent.

## CONCLUSION

The study shows that adsorption of cadmium from aqueous solutions on lateritic minerals can be achieved within a short contact time of 10 minutes without any prior chemical treatment or time-consuming adjustments. The reaction was found to be exothermic and occurs in the presence of a variety of ions, with maximum adsorption noted in the presence of 0.005 M  $\text{HNO}_3$ . The data generated can be useful in understanding the sorption mechanism and pathway of cadmium in lateritic profile during its migration in ecosystem. On the basis of this study, it is concluded that abundantly available inexpensive lateritic minerals, which finds little utility in general, has great potential to be used for the removal of cadmium from bulk aqueous solutions by making sieves or granules for their safe disposal.

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## REFERENCES

1. Daher, R.T. Trace metals (lead and cadmium exposure screening). *Anal. Chem.* **1995**, *67* (12), 405R–410R.
2. Antila, E.; Rauhamaa, H.M.; Kantola, M.; Atroshi, F.; Westermarck, T. Association of cadmium with human breast cancer. *Sci. Total Environ.* **1996**, *186* (3), 251–256.



3. Skogerboe, R.K.; Hanagan, W.A.; Taylor, H.E. Concentration of trace elements in water samples by reductive precipitation. *Anal. Chem.* **1985**, *57*, 2815–2818.
4. Nakashima, S.; Sturgeon, R.E.; Willie, S.N.; Berman, S.S. Determination of trace elements in sea water by graphite-furnace atomic absorption spectrometry after preconcentration by tetrahydroborate reductive precipitation. *Anal. Chim. Acta.* **1988**, *207*, 291–299.
5. Sugiyama, M.; Fujino, O.; Kihara, S.; Matsui, M. Preconcentration by dithiocarbamate extraction for determination of trace elements in natural waters by inductively-coupled plasma atomic emission spectrometry. *Anal. Chim. Acta.* **1986**, *181*, 159–168.
6. Khalid, N.; Chaudhri, Shamim A.; Saeed, M.M.; Ahmed, J. Separation and preconcentration of lead and cadmium with 4-(4-chlorophenyl)-2-phenyl-5-thiazoleacetic acid and its application in soil and seawater. *Sep. Sci., Technol.* **1996**, *31* (2), 229–239.
7. Hirata, S.; Honda, K.; Kumamru, T. Trace metal enrichment by automated on-line column preconcentration for flow-injection atomic absorption spectrometry. *Anal. Chim. Acta.* **1989**, *221*, 65–76.
8. Caroli, S.; Alimonti, A.; Petrucci, F. On-line preconcentration and determination of trace elements by flow injection-inductively coupled plasma atomic emission spectrometry. *Anal. Chim. Acta.* **1991**, *248*, 241–249.
9. Reed, B.E.; Arunachalam, S.; Thomas, B. Removal of lead and cadmium from aqueous waste streams using granular activated carbon columns. *Environ. Prog.* **1994**, *13* (1), 60–64.
10. Kozar, S.; Bilinski, H.; Branica, M.; Schwuger, M.J. Adsorption of Cd (II) and Pb (II) on bentonite under estuarine and seawater conditions. *Sci. Total Environ.* **1992**, *121*, 203–216.
11. Del-Debbio, J.A. Sorption of strontium, selenium, cadmium and mercury in soil. *Radiochim. Acta.* **1991**, *52/53*, 181–186.
12. Bermond, A.; Bourgeois, S. Influence of soluble organic matter on cadmium mobility in model compounds and in soils. *Analyst* **1992**, *117*, 685–687.
13. Garcia-Sosa, I.; Solache Rios, M. Sorption of cobalt and cadmium by mexican erionite. *J. Radioanal. Nucl. Chem.* **1997**, *218* (1), 77–80.
14. Rengan, K. Chelating resins: sorption characteristics in chloride media. *J. Radioanal. Nucl. Chem.* **1997**, *219* (2), 211–215.
15. Saha, B.; Iglesias, M.; Cumming, I.W.; Streat, M. Sorption of trace heavy metals by thiol containing chelating resins. *Solv. Extrac. Ion Exchange* **2000**, *18* (1), 133–167.



16. Abe, M.; Wang, P.; Chitrakar, R.; Tsuji, M. Adsorption and desorption behaviour of heavy metal ions on hydrated titanium dioxide. *Analyst* **1989**, *114*, 435–438.
17. Bhattacharyya, D.K.; Dutta, N.C. Immobilization of barium, cadmium and antimony cations over zirconia. *J. Nucl. Sci. Technol.* **1991**, *28*, 1014–1018.
18. Mishra, S.P.; Sing, V.K. Efficient removal of cadmium ions from aqueous solutions by hydrous ceric oxide-A radiotracer study. *Radiochim. Acta* **1995**, *68*, 251–256.
19. Mishra, S.P.; Tiwary, D. Inorganic particulates in removal of toxic heavy metal ions: efficient removal of cadmium ions from aqueous solutions by hydrous manganese oxide. *Radiochim. Acta* **1998**, *80*, 213–217.
20. Theis, T.L.; Iyer, R.; Kaul, L.W. Kinetic studies of cadmium and ferricyanide adsorption on goethite. *Environ. Sci. Technol.* **1988**, *22*, 1013–1017.
21. Balistrieri, L.S.; Murray, J.W. The adsorption of Cu, Pb, Zn and Cd on goethite from major ion seawater. *Geochim. Cosmochim. Acta* **1982**, *46*, 1253–1265.
22. Mahoney, J.J.; Langmuir, D. Adsorption of Sr on kaolinite, illite and montmorillonite at high ionic strength. *Radiochim. Acta* **1991**, *54*, 139–144.
23. Ahmad, S.; Qureshi, I.H. Fast removal of chromium from industrial effluents using a natural mineral mixture. *Intern. J. Environ. Anal. Chem.* **1991**, *41*, 257–264.
24. Ahmad, S.; Daud, M.; Khalid, N. Adsorption studies of radioactive silver using mineral mixture. *Radiochim. Acta* **1999**, *87*, 167–172.
25. Ahmad, S.; Khalid, N.; Daud, M. Adsorption studies of lead on lateritic minerals from aqueous media. *Sep. Sci. Technol.* **2002**, *37* (2), 343–362.
26. Ahmad, S.; Morris, D.F.C. Geochemistry of some lateritic nickel ores with particular reference of nobel metals. *Min. Mag.* **1978**, *42*, 143–161.
27. Ahmad, I.; Ahmad, S.; Morris, D.F.C. Determination of nobel metals in geological materials by radiochemical neutron activation analysis. *Analyst* **1977**, *102*, 17–24.
28. Ahmad, S.; Morris, D.F.C. Determination of several elements in lateritic ores by instrumental neutron activation analysis. *Analyst* **1977**, *102*, 395–399.
29. Dugger, D.L.; Stanton, J.H.; Irby, B.N.; McDonnell, B.L.; Cummings, W.W.; Maatman, R.W. The exchange of twenty metal ions with the weakly acidic silanol group of silica gel. *J. Phys. Chem.* **1964**, *68* (4), 757–760.



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30. Parks, G.A. The isoelectric points of solid oxides, solid hydroxides and aqueous hydroxo complex systems. *Chem. Rev.* **1965**, *65*, 177–198.
31. Mannan, A.; Ahmad, S.; Daud, M.; Qureshi, I.H. Europium removal with a mineral mixture. *J. Radioanal. Nucl. Chem., Artic.* **1992**, *157* (2), 347–353.
32. Music, S.; Gessner, M.; Wolf, R.H.H. Sorption of small amounts of europium(III) on iron(III) hydroxide and oxide. *J. Radioanal. Nucl. Chem.* **1979**, *50*, 91–100.
33. Faubel, W.; Sameh, A. A. Separation of cesium from ILW-purex solutions by sorption on inorganic ion exchangers. *Radiochim. Acta* **1986**, *40*, 49–56.
34. Benes, P.; Majer, V. *Trace Chemistry of Aqueous Solution*; Elsevier: Amsterdam, 1980; 200–223.
35. Qadeer, R.; Hanif, J.; Khan, M.; Saleem, M. Uptake of uranium ions by molecular sieve. *Radiochim. Acta* **1995**, *68*, 197–201.
36. Saeed, M.M.; Ghaffar, A. Adsorption syntax of Au(III) on unloaded polyurethane foam. *J. Radioanal. Nucl. Chem.* **1998**, *232*, 171–177.

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