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Adsorptive removal of cadmium by natural red earth: equilibrium and kinetic studies

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Natural red earth (NRE), an iron-coated sand found in the north western part of Sri Lanka, was used to examine the retention behaviour of cadmium, a heavy metal postulated as a factor of chronic kidney disease in Sri Lanka. Adsorption studies were conducted as a function of pH, ionic strength, initial Cd loading and time. The Cd adsorption increased from 6% to 99% with the pH increase from 4 to 8.5. The maximum adsorption was reached at pH > 7.5. Cadmium adsorption was not changed over 100-fold variations of NaNO₃, providing evidence for the dominance of an inner-sphere bonding mechanism for both 10-fold variation of initial Cd concentrations. Surface complexation modelling suggests a monodentate bonding mechanism. Isotherm data were fairly fitted to a two-site Langmuir isotherm model and sorption maximums of 9.11×10^{-6} and 3.89×10^{-7} mol g⁻¹ were obtained for two surface sites. The kinetic study reveals that Cd uptake by NRE is so fast that the equilibrium was reached within 15 min and ~ 1 h for 4.44 and 44.4 μ M initial Cd concentrations, respectively, and the chemisorption was the dominant mechanism over intra-particle diffusion. The study indicates the potential of NRE as a material for decontaminating environmental water polluted with Cd.

Keywords: natural red earth; adsorption; cadmium; isotherm; kinetics

Introduction

Heavy metals arising from anthropogenic and natural sources have the potential to cause adverse impacts on water quality and, consequently, human health when such water is consumed. The potential for adverse health effects caused by heavy metals can be seen at various locations throughout the world [1,2], including well-known arsenic poisoning in Bangladesh, Minamata disease [3] and the itai-itai disease in Japan [4]. Cadmium is considered as one of the most toxic heavy metals [5,6], with high mobility under slightly acidic conditions, since cadmium forms weaker aqueous and surface complexes than that of other metals [7]. The main environmental sources of cadmium are industries such as electroplating, smelting, battery, pigments, mining, alloy manufacturing and phosphate fertilizers [8]. Adverse health effects on humans due to cadmium include kidney failure, lung insufficiency, bone lesions, cancer and hypertension [9]. It is postulated that heavy metals (cadmium, lead) in agrochemicals is a major contributing factor to the chronic kidney disease [10] prevailed in some dry zone agricultural areas of Sri Lanka. Furthermore, Bandara et al. [10] reported that the dissolved cadmium in reservoir water of kidney disease prevalent areas of Sri Lanka ranged from 0.03 to 0.06 mg 1⁻¹, a 19-fold increase over maximum contaminant level set by the World Health Organization (WHO). Therefore, the need for an efficient and cost-effective material for treating cadmium in water is increasing.

The conventional methods for the removal of Cd from aqueous solutions are chemical precipitation, coagulation and filtration, ion exchange, adsorption on various materials, such as activated alumina, bone char, ion exchange resins, various hydrous Fe oxides and Mn oxides and biosorption [5,8,11,12]. Although these methods have varying degrees of effectiveness, the adsorption process seems to be the most versatile method, in terms of effectiveness and cost, for cadmium dissolved at low concentrations [8,13]. Most of the adsorption studies have been conducted on laboratory-synthesized material [7,8,13,14]. However, only a few have been carried out for natural soil materials [5,15]. Use of natural material for the removal of heavy metals is important for cost reduction of the removal methodology, especially for household use. Therefore, the particular study was based on natural red earth (NRE), a naturally occurring iron-coated sand [16], as a possible candidate for investigation as a low-cost water treatment material for Cd removal from water due to its complex surface composition.

As a low-cost alternative, we intend to use NRE for removal of low concentrations of contaminants from water. NRE would be effective in cost as it is freely available where mining activities occur. Since NRE is showing good absorption properties for arsenic species in water [16–18], there

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is an added interest in studying the adsorption behaviour of other heavy metals. Cadmium is selected due to the urgent need in Sri Lanka for removing cadmium from contaminated water. In this study, we intended to elucidate the sorption mechanism and examine the adsorption/desorption behaviour of the Cd through a series of batch experiments by ascertaining the effect of pH, initial Cd concentration and ionic strength.

Experimental details

Materials

NRE is abundantly found in the north western part of Sri Lanka, overlying the limestone strata, which is mined for the cement industry. NRE is considered as an iron-coated quartz sand with ilmenite and magnetite in minor amounts [17]. Recent X-ray diffraction analysis and X-ray fluorescence analysis indicated that NRE mainly consists of a silica phase, while Al (20.7% as Al₂O₃) and Fe (12.4% as Fe₂O₃) are also present in considerable amounts, probably as an amorphous coating to the extent that the surface properties of silica are masked completely as obtained from scanning electron microscopy (SEM) images. Therefore, only >AlOH and >FeOH sites, which abut from the surface amorphous coating, are considered to be active [16,18]. The mechanically sieved (using plastic sieves) finest sand fraction (63–180 µm) of NRE was used in this study.

All solutions were prepared with analytical grade chemicals (Wako, Japan) using Milli Q water. Metal nitrate salts were used to prepare stock solutions of metal ions. Ionic strength was adjusted with NaNO₃, and NaOH and HNO₃ were used to adjust the pH of the solution. Cadmium in solution was determined with a polarized Zeeman atomic absorption spectrophotometer equipped with a graphite furnace (HITACHI Z-5700, Japan), which has a detection limit of $0.2 \,\mu g \, l^{-1}$. A Fourier transform infrared (FTIR) spectrometer, Nicolet 6700, USA, was used for FTIR analysis.

Methods

Potentiometric titration experiment

A quantity of $10 \text{ g } \text{I}^{-1}$ NRE suspension was equilibrated for 2 h at a desired ionic strength prior to titration [7]. The initial pH of the suspension was about 6.5 and it was reduced to 4 using 0.096 M HNO₃ solution before the titration, and the suspension was titrated with 0.103 M NaOH solution to attain pH 10. Three titration experiments were carried out on the basis of different ionic strengths (0.1, 0.01 and 0.001 M NaNO₃). The surface charge was calculated according to Stumm and Morgan [19].

Adsorption edge experiments

Adsorption edges were carried out as a function of pH, ionic strength and adsorbate loading. The 500 ml of 5 g l^{-1} NRE

suspensions with desired ionic strengths (0.001, 0.01, 0.1 M NaNO₃) were prepared and equilibrated for 2 h. The pH of the solutions was adjusted to 4.0 using 0.5 M HNO₃ solution before the addition of Cd to yield final concentrations of 4.44, 8.89 and 44.4 μ M. The pH was then increased at 1 pH intervals up to pH 10 using 0.5 M NaOH solution and at each point a 20 ml sample was taken out into polypropylene centrifuged tubes. Samples were equilibrated for 24 h [7,16] at 200 rpm; this was followed by centrifugation (4000 rpm, 10 min) and filtration with a membrane filter (Millipore: 0.45 μ m), and the filtrate was then acidified for graphite furnace atomic absorption spectrometry (GF-AAS) analysis. Solution pH was measured again after equilibration. The experiments were conducted at 25 °C.

Adsorption isotherm and kinetic experiments

Cadmium adsorption isotherms were conducted in 0.01 M NaNO₃ solution, at pH \approx 7.5 and at 25 °C, based on the adsorption edge experiments. The pH adjustment was made with 0.5 M NaOH solution. The initial Cd concentrations varied between 8.8×10^{-8} and 4.44×10^{-4} M. The 500 ml of 5 g l⁻¹ NRE suspension was equilibrated for 2 h, and thereafter 20 ml aliquots were sampled into polypropylene centrifuge tubes. Desired amounts of Cd were spiked into the system, equilibrated for 24 h. The solid and the solution phases were separated under given conditions in adsorption edges.

The adsorption kinetics was studied for Cd loadings of 4.44, 8.89 and 44.4 μ M at 0.01 M NaNO₃ solution, at pH \approx 7.5 and at 25 °C. Cadmium was spiked into 500 ml of 5 g l⁻¹ NRE suspensions equilibrated for 2 h, and 10 ml samples were taken out at pre-determined time intervals. Sampling was carried out at 5 min intervals for the first 30 min, 10 min intervals for next 1 h and 30 min intervals thereafter, as the rate of adsorption decreased, and then reached the equilibrium. The samples were then immediately acidified and analysed for Cd.

All the experiments were carried out in triplicate and the average values are presented in the figures. The triplicate analyses have good reproducibility, with relative standard deviation of less than 10%.

Desorption experiments

The 500 ml of 5 g l⁻¹ NRE suspensions with 0.01 M NaNO₃ were prepared and equilibrated for 2 h. The pH of the system was adjusted to pH 7.5 and Cd was spiked into the system to achieve the final concentration of 4.44 μ M. The system was equilibrated for 24 h at 25 °C at 200 rpm. Samples of 20 ml were taken into centrifuge tubes. After centrifugation, the supernatants were used for Cd adsorption measurements. Residues were washed three times with 0.01 M NaNO₃ and 20 ml of 0.01 M NaNO₃ solution adjusted to pH 1–10 was added to them. The suspensions were equilibrated for 24 h in similar conditions to those in the previous experiments.

The final pH was measured, and then the suspensions were centrifuged and filtered. The filtrates were used for Cd desorption measurements.

FTIR determination

The FTIR spectrograms of vacuum-dried NRE sample pellets, prepared with fused KBr, were obtained with a resolution of 1 cm^{-1} between 400 and 4000 cm⁻¹. The spectrums were analysed using OMNIC version 7.3 software.

Data modelling

The potentiometric titration and adsorption edge data were interpreted by a surface complexation model in conjunction with a generalized diffuse double-layer model (DLM) and 2pK approach using the FITEQL computer algorithm [20]. The 2-pK approach is widely used for metal (hydroxyl) oxides and in this case the surface is hydroxylated in two steps: > SOH + H⁺ \rightarrow > SOH₂⁺ and > SOH \rightarrow > SO⁻ + H⁺ [16,21–23]. The generalized DLM was selected due to its simplicity, applicability to different solution conditions, capability of handling several surface sites simultaneously, incorporation of high inner layer capacitance and low outer layer capacitance representation in a single surface layer of the DLM and use of the Gouy–Chapman theory [19,22]. Hence, this provides a good platform for the estimation of surface and adsorption properties of NRE.

As the mineral phase of NRE is completely masked by the amorphous coating, the active surface sites of NRE, >FeOH and >AlOH, were selected for modelling [16–18]. It was assumed that the two surface sites are nonequivalent [16,24,25]. The cation exchange capacity (CEC) of NRE was as low as 18 meg/100 g soil, hence Cd retention by an ion exchange mechanism was not considered [16,18]. Based on the log K of surface protonation (FeOH + $H^+ \Leftrightarrow FeOH_2^+$, $AlOH + H^+ \Leftrightarrow AlOH_2^+$) and deprotonation (FeOH \Leftrightarrow FeO⁻ + H⁺, AlOH \Leftrightarrow AlO⁻ + H⁺) values obtained by Vithanage et al. [16], potentiometric titration data were optimized. The optimized values obtained from potentiometric titration for surface area, protonation and deprotonation constants and site densities were used for optimization of the Cd adsorption constants. Four aqueous species, Cd²⁺, CdOH⁺, Cd(OH)₂⁰, CdCO₃ and the carbonate dissociation constants, were considered for model calculations [26,27]; metal solution phase reactions and equilibrium constants used for the model [22] are given below:

$Cd^{2+} + OH^{-} \Leftrightarrow CdOH^{+}$	$\log K = 3.9$
$Cd^{2+} + 2OH^- \Leftrightarrow Cd(OH)_2^0$	$\log K = 7.6$
$\mathrm{Cd}^{2+} + \mathrm{CO}_3 \to \mathrm{Cd}\mathrm{CO}_3$	$\log K = 5.40$
$\mathrm{CO}_3^{2-} + 2\mathrm{H}^+ \Leftrightarrow \mathrm{H_2CO_3}$	$\log K = 6.35$
$\mathrm{CO}_3^{2-} + \mathrm{H}^+ \Leftrightarrow \mathrm{HCO}_3^-$	$\log K = 16.68$

Isotherm data were fitted to the two-site Langmuir equation and kinetic data were treated with four kinetic models.

Results and discussion

Potentiometric titration and surface area

Surface complexation parameters (site densities and pHpzc (point of zero charge)) of the NRE surface were obtained from the potentiometric titration in the absence of the metal ion. Figure 1 shows the surface charge of NRE suspension and the common intersection point of the titration curves obtained for 0.1, 0.01, 0.001 M NaNO₃. Since the pHpzc is not affected by the concentration of the inert electrolyte [19], the pHpzc was established as the pH of the common intersection point of the curves and the experimentally estimated pHpzc of the NRE suspension (63–180 µm fraction) was 6.6. The relative shift of the common interception point from the isoelectric point (pH where the surface carries no net electrical charge) could be discussed as the asymmetrical ion pair formation and the difference of the affinity between the cation and the anion of the background salt [28]. However, NaNO₃ is a commonly used electrolyte with the least difference of the affinity of ions for adsorption studies [7,16,19,28]. FITEQL optimized data (lines in Figure 1) matched with experimental data of potentiometric titration (symbols in Figure 1). The surface titration reactions assumed were protonation and deprotonation of variable charge sites (>SOH) and it is evident that the surface sites are amphoteric. The proton affinity constants and site concentrations of two sites of the NRE (>FeOH and >AlOH) surface were assumed to be different; the values obtained by FITEQL numerical optimization and the reaction stoicheometries are given in Table 1. The >FeOH sites and >AIOH sites ratio was converged around 250:1 by the model, which was fairly consistent with that for $<63 \,\mu m$



Figure 1. Variation of surface charge as a function of pH.

	Value				
Parameter	0.1 M NaNO ₃	0.01 M NaNO ₃	0.001 M NaNO3	Weighted mean	
Site density					
FeOH	1.25×10^{-1}	8.07×10^{-2}	8.20×10^{-3}	8.08×10^{-2}	
AlOH	3.02×10^{-4}	2.82×10^{-4}	2.87×10^{-4}	$2.97 imes 10^{-4}$	
Log K					
Protonation reactions					
$FeOH + H^+ \Leftrightarrow FeOH_2^+$	3.06	3.49	4.97	3.38	
$FeOH \Leftrightarrow FeO^- + H^+$	-11.11	-11.15	-10.15	-10.93	
$AIOH + H^+ \Leftrightarrow AIOH_2^+$	9.88	10.07	9.49	9.52	
$AIOH \Leftrightarrow AIO^- + H^+^2$	-8.39	-9.42	-8.03	-8.14	
Surface reactions					
$FeOH + Cd^{2+} \Leftrightarrow FeOCd^+ + H^+$	8.75	8.40	8.50	8.54	
$AlOH + Cd^{2+} \Leftrightarrow AlOCd^+ + H^+$	13.84	14.00	13.94	13.92	

Table 1. Generalized diffused layer parameters for Cd adsorption onto NRE optimized using FITEQL.

The log K values are the weighted averages calculated using $\log K = \sum \omega_i (\log K)_i$, where $\omega_i = (1/\sigma_{\log K})_i / \sum (1/\sigma_{\log K})_i$, where $\sigma_{\log K}$ is the standard deviation obtained from FITEQL calculations.

NRE fraction [16,24,25]. The sensitivity analysis was conducted by varying the values of site density in the FITEQL input file and observing the effect on the optimized values of the surface protolysis constants, as indicated by Hayes *et al.* [29]. The surface protolysis constants, which fit better with the titration curves with lower F values, were taken as log $K_{\text{protonation}}$ and log $K_{\text{deprotonation}}$. While the intrinsic constants obtained for two sites were comparable with those obtained by Vithanage *et al.* [16], the pHpzc attained from model calculations was 6.3, which was analogous to the value, 6.6, obtained by the titration experiment (Figure 1).

The surface area for the selected NRE fraction estimated by data modelling was $260 \text{ m}^2 \text{ g}^{-1}$. The estimated specific area for the $< 63 \mu \text{m}$ fraction by Vithanage *et al.* [18] was $350 \text{ m}^2 \text{ g}^{-1}$. Since the fraction selected for this study is higher than that of Vithanage *et al.* [18], the estimated surface area is assumed to be sufficient.

Adsorption edges

The pH of the solution is an important variable governing the metal ion adsorption, as it affects the surface charge of the sorbent and the speciation of pollutants. Cadmium adsorption increased from 6% to 99% with the pH increased from 4 to 8.5 with maximum adsorption at pH > 7.5. The experimental results are shown in Figure 2 (by symbols). The shape of the adsorption edge is sigmoid. A rapid adsorption occurs within a narrow pH range between 6.0 to 7.5 when the initial Cd concentration is 4.44 μ M (Figure 2(a)). This is the pH where the positive variable charge sites of the NRE surface becomes negative (pHpzc = 6.6). When the initial Cd concentration is 44.4 μ M, the adsorption edge has broadened from pH 5.6 to 7.0 (Figure 2(b)). Once the initial Cd concentration increased, the adsorption edge shifted to



Figure 2. Variation of cadmium adsorption onto NRE as a function of pH and ionic strength. (a) $4.44 \,\mu mol \, l^{-1}$ [Cd]_{initial}. (b) $44.4 \,\mu mol \, l^{-1}$ [Cd]_{initial}. Lines represent double-layer model calculations, while symbols represent experimental data.

a lower pH. The pH_{50%} value indicates that the pH values corresponding to 50% adsorption at 4.44, 8.89 and 44.4 μ M of initial Cd concentrations are 6.71, 6.42 and 6.45, respectively. As discussed by Weerasooriya *et al.* [7], the relative shift of the adsorption edges with the adsorbate loading implies that the initial concentrations are set to fall in the non-linear region of the isotherm. Our isotherm data proves that these initial Cd concentrations lie in the non-linear region of the isotherm.

According to Stumm and Morgan [19], mechanisms of surface complexation are evidenced by ionic strength dependence of adsorption edges. Outer-sphere complexes strongly depend on the ionic strength and, therefore, yield distinctly separated adsorption edges for different ionic strengths, while such an observation cannot be made for inner-sphere complexes. Figures 2(a) and (b) (by symbol), which indicate the effect of ionic strength on the change of Cd adsorption with increasing pH for both 4.44 and $44.4\,\mu$ M initial Cd concentrations, do not show any ionic strength dependency for 100-fold variations of NaNO₃. This fact may suggest the dominance of an inner-sphere bonding mechanism for 10-fold variations of initial Cd concentration. However, this is an indirect method for distinguishing inner-sphere and outer-sphere complexes [30] and ambiguity exists when adsorbing ions of intermediate affinity [31].

Cadmium adsorption modelling on the NRE surface was carried out with a generalized diffuse layer model. The >FeOH and >AlOH site ratios were kept as 250:1 as converged for surface titration modelling. As Dzombak and Morel [22] discussed, the positively charged species >FeOM⁺ fitted transition metal cation adsorption onto hydrous ferric oxide; therefore, monodentate surface complexation reactions $FeOH + Cd^{2+} \Leftrightarrow FeOCd^+ + H^+$ and $AIOH + Cd^{2+} \Leftrightarrow AIOCd^+ + H^+$ were considered for data modelling. The modelling results fitted well the experimental results, especially for adsorption edges of 4.44 µM initial Cd loading. Modelled data are shown by the solid, dotted and dashed lines in Figure 2. The optimized Cd binding constants (for 4.44 µM initial Cd concentration) are given in Table 1. With ionic strength, independent Cd adsorption, and modelling, we postulate a monodentate chemical bonding mechanism for Cd binding onto two different sites of the NRE surface.

Adsorption isotherm

The adsorption isotherms provide an understanding of the distribution of chemicals in solid and aqueous phases at the equilibrium. These were constructed for the 0.088–444 μ M initial Cd concentrations, at pH \approx 7.5 and ionic strength 0.01. According to the initial slopes and curvature, the isotherm obtained could be classified as an L-type isotherm [32], where the sorbate is strongly attracted by the sorbent. As observed by Vithanage *et al.* [16], NRE consists of two surface sites, >FeOH and >AIOH. The Cd



Figure 3. Adsorption isotherm of cadmium adsorption onto NRE.

adsorption modelling data reported in this paper further confirmed the presence of two surface sites of different affinities. Therefore, the isotherm data were treated with the two-site Langmuir isotherm (Equation (1)) [19]. The data fitting obtained for the two-site Langmuir isotherm equation is shown in Figure 3.

$$\Gamma = \frac{\Gamma_1 K_1[A]}{1 + K_1[A]} + \frac{\Gamma_2 K_2[A]}{1 + K_2[A]}$$
(1)

where Γ is Cd adsorption per g solid, K_1, K_2 are Langmuir equilibrium adsorption constants and Γ_1, Γ_2 are Langmuir constants associated with maximum adsorption capacity for two sites of NRE.

The two-site Langmuir model fits experimental data with 0.977 correlation coefficient and 3.37×10^{-13} chisquared values. The values obtained for model parameters were $2.41 \times 10^4 \text{ L mol}^{-1}$, $9.93 \times 10^6 \text{ L mol}^{-1}$, $9.11 \times 10^{-6} \text{ L mol} \text{ g}^{-1}$, and $3.89 \times 10^{-7} \text{ L mol} \text{ g}^{-1}$ for K_1, K_2 and Γ_1 , Γ_2 , respectively. The two-site Langmuir equation assumes monolayer adsorption of adsorbate onto adsorbent with two sites of different affinities [19]. Therefore, the twosite Langmuir fit suggests Cd adsorb strongly onto the both sites of >FeOH and >AIOH as a monolayer. The positively charged Cd²⁺ may adsorb readily onto negatively charged sites or neutral sites.

In this system, the highest concentration of Cd was less than 0.5 mM (444 μ M). In addition, the equilibrium pH of the higher concentration of the particular system was lower than pH 4. The speciation diagram indicates that only the Cd²⁺ ion is dominant in the pH range of 4–9, and both CdOH⁺ and Cd(OH)⁰₂ become significant at pH > 10 [7,25]. In an open system CO²⁻₃ ion concentration reaches 10^{-6} M at the pH > 8. Venema *et al.* [33] have observed that precipitation of CdCO₃ occurs when the Cd concentration is higher than 0.5 mM. Therefore, even at the higher concentration of Cd, precipitation of Cd as Cd(OH)₂ and $CdCO_3$ was not possible in our system and therefore not taken into account. Thus, only the positively charged Cd^{2+} species is thought to be adsorbed dominantly onto NRE.

Adsorption kinetics

The adsorption kinetics were studied to determine the time required to achieve the equilibrium. The experiments were carried out for initial Cd concentrations $4.44 \,\mu\text{M} \,(500 \,\mu\text{g}^{-1}), 8.89 \,\mu\text{M} \,(1000 \,\mu\text{g}\,\text{l}^{-1})$ and $44.4 \,\mu\text{M} \,(5000 \,\mu\text{g}\,\text{l}^{-1})$. The data reveal that Cd uptake by NRE is fast and reaches the apparent plateau within the first 15 minutes for $4.44 \,\mu\text{M}$ initial Cd concentration, while it was nearly one hour for 8.89 and $44.4 \,\mu\text{M}$ initial Cd concentrations (Figure 4(a) by symbols). This shows that the experimental equilibration period is sufficient for Cd adsorption. However, the system was equilibrated 2 h before the addition of Cd, to allow the system to undergo hydration and hydroxylation [22].



Figure 4. Kinetics of Cd adsorption onto NRE. (a) Cd adsorption as a function of time. (b) Pseudo second-order plot. Lines represent the calculated values, while symbols represent experimental data.

The adsorbate transferring process from solution to the adsorbent surface could be controlled by one or more steps, such adsorption onto surface, external diffusion and pore diffusion [34]. Therefore, the kinetic data were treated with a pseudo first-order model, a pseudo second-order model, an intra-particle diffusion model and Vermeulen approximation to trace the adsorption process. The conformity between experimental data and the model predicted values was expressed by correlation coefficient (R^2) and a chi-square (X^2) test.

Figure 4(a) shows Cd adsorption on NRE as a function of time. The integrated forms of the pseudo first-order model and pseudo second-order model were used for data fitting, as integrated forms describe the particular equation in detail [8,31]. The kinetic parameters obtained from three kinetic models and the equations of the models are listed in Table 2. The results reveal that the pseudo second-order model fitted better with experimental data than the pseudo first-order model and intra-particle diffusion model with higher R^2 (≈ 1) values and lower X^2 values (Table 2). The time verses t/qt plots drawn for the pseudo second-order model for three initial Cd concentrations are shown in Figure 4(b). Straight lines passing through the origin were obtained for three initial Cd concentrations. The q_{exp} (amount adsorbed per g of the adsorbent at equilibrium from experimental data) and q_{cal} of the pseudo second-order model (amount adsorbed per g of the adsorbent at equilibrium calculated by the model) are consistent with each other. Figure 4(a)also gives Cd adsorptions obtained by calculation based on pseudo second-order model by lines, which are in good agreement with the experimental data (by symbols) for all initial Cd concentrations considered. The pseudo secondorder model reveals that the rate of adsorption is low when it reaches equilibrium and some authors discussed that the particular model is an indication of chemisorption mechanisms [8,35]. Trivedi and Axe [36] described a two-step process for metal ion retention on hydrous oxides: a rapid adsorption preferably due to the external surfaces followed by a slow retention due to intra-particle diffusion along the micro pore walls utilizing internal surfaces. In this study, as the adsorption of Cd onto NRE is a rapid process, the external surfaces of NRE are expected to be involved in the adsorption process. Moreover, the C values (a constant representing boundary layer effect) of the intra-particle diffusion model are very small and have been increased with increasing Cd concentrations (Table 2). This means that the boundary layer effect is very small for all three initial Cd concentrations, even though the effect increases with increasing Cd concentrations.

Further, the kinetic data were treated by Vermeulen's approximation (Equation (2)) [37], which is a simplified version of the diffusivity model proposed by Boyd *et al.* [38]:

$$\ln\left[\frac{1}{1-F^2(t)}\right] = \frac{\pi^2}{R_a^2} D_e t \tag{2}$$

Pseudo fir Equation	st-order parameters $\frac{dq}{dt} = K_1(q_e - q_t)$		Integrated form $\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303}$			
C ₀ (μM)	q_{\exp} (µmol g ⁻¹)	q_{cal} (µmol g ⁻¹)	$\frac{K_1}{(\min^{-1})}$	R^2	<i>X</i> ²	
4.44 8.89 44.4	0.822 1.322 2.841	0.272 0.385 1.701	0.379 0.047 0.051	0.984 0.937 0.986	1.575 27.85 23.84	
Pseudo see Equation	cond-order parameters $\frac{dq}{dt} = K_2(q_e - q_t)^2$	5	Integrated form $\frac{t}{q_t}$ =	$=\frac{1}{K_2q_e^2}+\frac{t}{q_e}$		
C ₀ (μM)	q_{\exp} (µmol g ⁻¹)	$q_{ m cal}$ (µmol g ⁻¹)	$\frac{K_2}{(g\mu\text{mol}^{-1}\text{min})}$	R^2	<i>X</i> ²	
4.44 8.89 44.4 Intra-parti	0.822 1.322 2.841 cle diffusion model pa	0.824 1.335 2.916 arameters	5.877 0.421 0.822	0.999 0.999 0.999	0.007 0.949 2.941	
Equation q	$q_t = K_{\mathrm{id}}t^{0.5} + C$					
$\frac{C_0}{(\mu M)}$	$q_{\exp} (\mu mol g^{-1})$	$q_{cal} \ (\mu mol g^{-1})$	$C \pmod{(\mu \mod g^{-1})}$	$\frac{K_{id}}{(\mu \text{mol g}^{-1} \min^{0.5})}$	R^2	<i>X</i> ²
4.44 8.89 44.4	0.822 1.322 2.841	1.718 1.703 5.531	0.570 0.817 0.925	0.519 0.847 1.201	0.883 0.943 0.975	39.349 52.313 71.044

Table 2. Kinetic parameters for the removal of Cd by NRE.

 q_e – amount adsorbed per g of the adsorbent at equilibrium (μ M g⁻¹), q_t – amount adsorbed per g of the adsorbent at time t (μ M g⁻¹), t – time in minutes, C_0 – initial concentration of Cd in solution, q_{exp} – amount adsorbed per g of the adsorbent at equilibrium calculated from experimental data, q_{cal} – amount adsorbed per g of the adsorbent at equilibrium calculated from model calculations, K_1 – Lagergren rate constant, K_2 – pseudo second-order constant, K_{id} – intra particle diffusion rate constant, C – constant represents boundary layer effect, R^2 – correlation coefficient and X^2 – chi-square.

where F(t) denotes q_t/q_e , which is fractional attainment of the equilibrium at time t, D_e denotes the effective diffusion coefficient of adsorbates in the adsorbent phase (m² s⁻¹) and R_a is the radius of the adsorbent particle (m). The D_e values obtained by the slopes of the plots time verses $\ln[1/(1 - F^2(t))]$ are 9.13×10^{-12} , 1.04×10^{-12} and 1.19×10^{-12} m² s⁻¹ for 4.44, 8.89 and 44.4 μ M initial Cd concentrations, respectively. The high D_e value is due to diffusion within the wider pores and weaker retarding forces of electrostatic interactions. These values lie within the values considered as chemisorption systems (from 10^{-9} to 10^{-17} m² s⁻¹) [8].

Desorption of Cd

During adsorption, 98% of $4.44 \,\mu$ M Cd has been adsorbed onto NRE at pH 9. Cadmium desorption increased with reducing pH and all Cd adsorbed was desorbed below pH 2. Desorption was rapid when the pH was lower than 4, probably due to the dissolution of soil. However, after the desorption at pH 4, 33% of adsorbed Cd was retained on the NRE surface. The adsorption edges indicated 12% adsorption at pH 4, 0.01 M NaNO₃ for similar initial loading. Therefore, it can be argued that desorption of Cd is not completely reversible. This implies the high affinity of Cd binding on the NRE surface, which is suitable for the soil to be used as a pollutant removal material in the natural pH range (pH 5–7). Since all Cd is desorbed in lower pH, it overcomes the problem of disposal of Cd-loaded NRE and allows recovery of metal ions in the concentrated solution.

FTIR spectrum determination

FTIR experiments were carried out for 44.4 and 4.44 μ M initial Cd concentrations, 0.01 of ionic strength at initial pH values 4 and 9. The spectrum illustrated two specific spectral regions in 3000–4000 cm⁻¹ and 400–1750 cm⁻¹. The 3000–4000 cm⁻¹ region corresponds to the stretching and bending vibration of the hydroxyl group. The peak is centred at 1630 cm⁻¹ and is ascribed to OH bending vibration [39]. The peaks observed at 650–1250 cm⁻¹ are assigned to metal oxide bonds [16].

Upon Cd adsorption, changes were expected to be detected in the surface hydroxyl region of $3000-4000 \text{ cm}^{-1}$. Three bands centred around 3460, 3620 and 3400 cm⁻¹ were observed for bare NRE. The deconvolution



Figure 5. FTIR spectra of aqueous suspension of NRE. (a) Curve decomposition for bare NRE. (b) Curve decomposition for Cd-treated NRE (Cd initial concentration $44.4 \,\mu$ M).

technique was employed to spectral data in the region of $3000-4000 \text{ cm}^{-1}$, as the actual number of bands cannot be counted due to lack of symmetry around band centres and consistency of shoulders. Deconvolution resulted in seven bands (peak/full width at height maximum (FWHM)) at 3699/24, 3673/11, 3657/20, 3646/21, 3622/20, 3465/288 and 3238/350 for bare NRE (Figure 5(a)). Upon the presence of Cd, 3238 and 3465 cm⁻¹ bands have shifted to lower wave numbers (3460/302, 3212/317 and 3460/313, 3204/340 for 4.44 and $44.4\,\mu M$ initial Cd concentrations, respectively), disappearing at 3673 cm⁻¹ in 44.4 μ M Cd (Figure 5(b)). The disappearing band is ascribed to structural hydroxyls [40]. Bands shifting to lower wave numbers indicate the occurrence of more surface hydroxyl groups. The area intensities of 3238, 3465 cm^{-1} have been decreased, while 3622 and 3646 cm⁻¹ increased with Cd adsorption. As discussed by Ece et al. [39], Sposito and

Prost [41] and Bertie et al. [42], the 3622 cm⁻¹ band could be ascribed to strong OH stretching vibration, while the 3465 cm^{-1} band is due to H₂O stretching and H-bonding. Appearance or disappearance of peaks was not observed in the metal oxide region. However, band intensities and shifting could be seen. Band shifting to high wave numbers in the metal oxide region indicates strong bond formation with metal ions on the surface with Cd in the solution. The band appearing at 913 cm^{-1} , which is ascribed to >Al-O-H vibration [16,39], becomes intense with Cd treatment. This could be an indication of the formation of a >Al-O-Cd bond. The band 1035 cm^{-1} , which is described as a corresponding band for Fe³⁺ substitution in tetrahedral layers in Fe-montmorillonite [39], was also observed for NRE. This particular band intensity was also increased with increasing Cd concentration upon Cd adsorption. This could be due to the Cd adsorption onto Fe sites. With decreasing

H₂O stretching and H-bonding and increasing OH stretching, shifting of bands to high wave numbers in the metal oxide region and no new band formation, it is suggested that Cd adsorption onto NRE is based on an inner-sphere monodentate bonding mechanism.

Conclusion

NRE, a low-cost material, which is abundantly found in the north western province of Sri Lanka and discarded after limestone mining, was used for this study. NRE showed good results for Cd adsorption. Optimum results for Cd removal were found at pH \approx 7.5. The equilibrium between adsorbate and adsorbent was achieved in 1 h for the highest concentration of adsorbate selected. The adsorption data fitted well with the diffuse layer model and these findings showed that Cd was adsorbed onto NRE effectively. The bonding mechanism drawn from chemical modelling in inner-sphere monodentate formation and FTIR analysis further supports the bonding mechanism. NRE is promising material as a low-cost adsorbent for Cd removal in water.

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