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Competitive Adsorption of Nickel and Cadmium on Sheep Manure Wastes: Experimental and Prediction Studies

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ABSTRACT

Sheep manure wastes (SMW) previously have been shown to be very efficient in removing nickel and cadmium from single-component, dilute aqueous solutions. Simultaneous removal of nickel and cadmium ions from aqueous solutions using SMW has been investigated in this study. The experimental results showed that the SMW has a relatively higher affinity for cadmium binding than that for nickel. Different multicomponent-isotherm models; extended Langmuir, modified Langmuir, extended Redlich–Peterson, and extended Sips isotherm models, were used to predict the removal of either ions using single metal isotherm data.

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Key Words: Adsorption; Nickel; Cadmium; Heavy metals; Manure; Isotherm.

INTRODUCTION

Industrial water is one of the major sources of aquatic pollution. Aquatic pollutants include organic compounds, pathogens, and heavy metals. Among these pollutants, heavy metals have gained relatively more significance in view of their persistence and toxicity. Heavy metals are defined as metals that have specific gravity greater than about 4 or 5, but more often, the term heavy metals is simply used to denote metals that are toxic.[1] Many studies have shown that these metals are toxic, even at low concentrations. These toxic metals can cause accumulative poisoning, cancer, and brain damage when found above the tolerance levels.[2] Exposure to nickel can cause dermatitis and allergic sensitization.[3] The harmful effects of cadmium include a number of acute and chronic disorders, such as renal damage, emphysema, hypertension, and testicular atrophy.[4] Having in mind the harmful effects of the heavy metals, environmental agencies set permissible limits for their concentrations in drinking water and set strict regulations to restrict their careless discharge from industrial plants.

Heavy metal contamination exists in the effluent wastewater from different industries, such as metal processing, photography, ceramic industry,[5] metal plating, mining operation, radiator manufacturing, alloy industries and storage batteries manufacture,[6] catalyst, electrical apparatus, extractive metallurgy, antibacterial, insecticides, fungicides, pyrotechnics, fertilizers, pigments, stabilizers, plumbing, roofing and building construction, piping, water purification, gasoline additives, and cable covering.[7,8] The heavy metals concentration in the industrial wastewater from these industries should be decreased to the permissible limits; therefore the ground water will not be affected. Chemical precipitation, coagulation, solvent extraction, membrane separation, ion exchange, and adsorption are commonly applied in the treatment of industrial effluents.[9] Precipitation has been the most common technology for metals removal; however, it can only reduce the dissolved metal concentration to the solubility levels. For dilute metal concentrations, ion exchange, reverse osmosis, and adsorption can be applied.[10] Ion exchange and reverse osmosis have high operating costs; however, which makes adsorption the first choice for metal removal.

Adsorption is a mass transfer process that involves the contact of a solid (adsorbent) with a fluid containing certain components that are transferred and physically or chemically attached to the surface of the adsorbent. Activated carbon is one of the most common adsorbents for heavy metals, but its high capital and regeneration cost encouraged researchers to seek for new available and cheap adsorbent. Many different adsorbents have been investigated to adsorb heavy metals. The utilization of microbial biomass for the removal of heavy metals from wastewater has already been recognized. There are large numbers of microorganisms reported in literature for the adsorption of metals, for example, *Rhizopus arrhizus* was examined to adsorb Cu^{2+} and Zn^{2+} from wastewater[11] and *Streptomyces rimosus* was studied to adsorb Zn^{2+} from aqueous solutions.[12] Researchers have also studied agricultural products and by-products or wastes for the removal of heavy metals from aqueous solutions. Soy bean hulls were examined to adsorb Cu^{2+} from aqueous solution.[13] Sunflower stalks were studied to remove Cu^{2+}, Cd^{2+}, Zn^{2+}, and Cr^{3+}.[14] Chatterjee et al.,[15] Hequet et al.,[16] and Apak et al.[17] studied the use of fly ash to remove heavy metals from aqueous solution. Sheep manure waste (SMW) is a new low-cost adsorbent that has been proved to be effective for heavy metal ions.[18,19] SMW consists of different biomaterials that may be responsible for the uptake of metal ions. The main constituents present in SMW are proteins, cellulose, hemicellulose, and lignin.

The objective of the present work is to study the competitive adsorption of cadmium–nickel binaries on SMW experimentally and theoretically. The adsorption isotherms of the binary system will be predicted using the adsorption isotherms of the single metals. The predicted results will be compared with the experimental ones.

EXPERIMENTAL

Adsorbent

Sheep manure waste (SMW) used in this work was collected from one farm in a town in the north of Jordan. The collected SMW was washed with distilled water, dried, ground, and sieved to obtain four particle sizes in the range of 0.063–1.000 mm. Finally, the SMW was heated at 105°C for 2 hours to remove any volatile materials that may have existed in the SMW. The processed SMW was analyzed according to the following standard methods.

Apparent Density

Apparent density of SMW was determined according to the ASTM methods: 10.0 g (dry basis) of SMW was weighed, one third of the weighed sample was transferred to 100-mL graduated cylinder, and, while gently, tamping on a rubber pad, SMW was added until the entire weighed sample was transferred. Tamping was continued for 5 minutes until there was no further settling produced. The volume was recorded and the apparent density was calculated on the dry basis:

$$\text{Apparent density} = \frac{\text{weight of the sample (g)}}{\text{volume of the sample (L)}}$$

Iodine Number

The iodine number is defined as the milligrams of iodine adsorbed by 1 g of the adsorbent when the iodine concentration of the residual filtrate is 0.02 N. Iodine number is generally applied as fast industrial test for assessing the quality of the adsorbent. It gives information about the internal surface of the adsorbent; 1.0 mg of the iodine adsorbed is considered to represent 1.0 m^2 internal surface.[20] In this work, the iodine number was obtained according to ASTM methods.

Ash Content

One gram (dry basis) of the sample was transferred into a clean, dry crucible. The crucible with its content was weighed. The crucible then was placed in a furnace and the temperature was raised to 973 K. After 4 hours, the crucible was cooled to room temperature and weighed. Then the ash content was calculated:

$$\text{Ash content (\%)} = \frac{\text{weight of the ash (g)}}{\text{weight of the original sample (g)}} \times 100\%$$

Adsorbent pH

A suspension of 1.0 g of the SMW in 20.0 mL of carbon dioxide-free distilled water at 298 K was prepared. After shaking for 48 hours, the suspension pH was measured using a digital pH meter and recorded.

Table 1. Characteristics of SMW.

Apparent density, g/mL	0.588
Ash content, %	31.6
Iodine number	948.2
Moisture, %	4.7
Crude protein, %	15.4
NDF, %	36.92
ADF, %	28.2
Average particle size, mm	0.064
pH	7.24

Proximate Analysis

Proximate analysis concerns the determination of the percentage composition of the plant material. Structurally, plant materials consist of lignin, cellulose, hemicellulose, and protein. In this study, the method of Association Official Analytical Chemists (AOAC) was used in proximate analysis. SMW was boiled in a neutral detergent solution. The soluble fraction is termed neutral detergent soluble, NDS (cell contents), while the fibrous residue is called neutral detergent fiber, NDF (cell wall constituents). Cell wall constituents were further boiled in acidic detergent solution where the soluble fraction is primarily hemicellulose. The insoluble fraction is termed ADF. Table 1 shows the characteristics of the processed SMW used in this study.

Chemicals

Metal ion solutions were prepared by diluting 1000-ppm stock metal solutions. Stock solutions were prepared from $N_2NiO_6{\cdot}6H_2O$ for nickel ions and $3CdSO_4{\cdot}8H_2O$ for cadmium ions. Initial pH was adjusted by diluted hydrochloric acid or diluted sodium hydroxide.

Procedure

Solutions of each metal's ions at different initial concentrations were prepared. The two metal ion solutions were mixed to prepare different concentrations of the binary metal solutions. A certain amount of SMW was transferred into 100 mL reagent bottles containing 50 mL of the binary solution. For each initial concentration, several bottles were shaken in a reciprocating shaker; samples were taken at certain periods of time. SMW was separated from the samples by filtration using (WHATMAN filter paper No. 4) and the supernatant was analyzed for both metal ions using a Verian (Spectra AA-10/20) atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Experimental Results of Adsorption of Ni^{2+}–Cd^{2+} System

The effect of the presence of Cd^{2+} on the uptake of Ni^{2+} is shown in Fig. 1, which indicates that Ni^{2+} uptake was suppressed in the presence of cadmium ions. The decrease in nickel uptake, as shown in Fig. 1, is a function of the initial concentration of the cadmium ions; as the cadmium ions initial

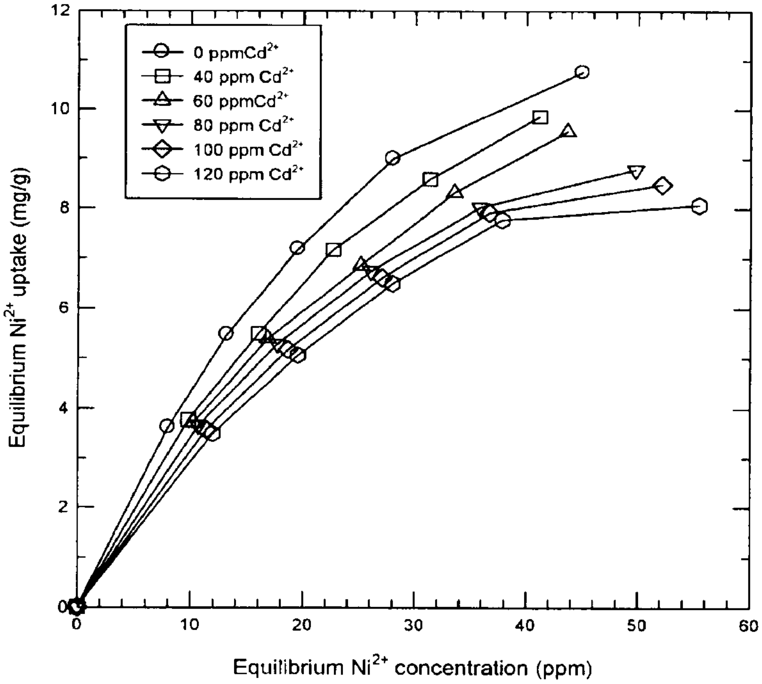


Figure 1. Effect of the presence of Cd^{2+} on the adsorption of Ni^{2+} in (Cd^{2+}–Ni^{2+}) binary system. Initial Ni^{2+} concentration = 40–120 ppm, and initial Cd^{2+} concentration = 0–120 ppm.

concentration increases, nickel uptake decreases. This decrease in the equilibrium uptake can be contributed to the competition between nickel and cadmium. Figure 2 shows the effect of the presence of nickel ions on cadmium uptake. As shown by this figure, the presence of nickel ions also resulted in a decrease in cadmium uptake. This decrease is a function of the nickel ions initial concentration. However, the decrease in nickel uptake in the presence of cadmium is relatively more than that for cadmium uptake in the presence of nickel. This is because the affinity of Cd^{2+} for SMW, as found from results of adsorption of single metals on SMW,[18,19] is higher than that of the nickel.

To investigate the mechansim(s) of adsorption of Ni^{2+} and Cd^{2+} on SMW, the contribution of the ion exchange mechanism and the carboxyl group in the adsorption on SMW was studied. The ion exchange mechanism

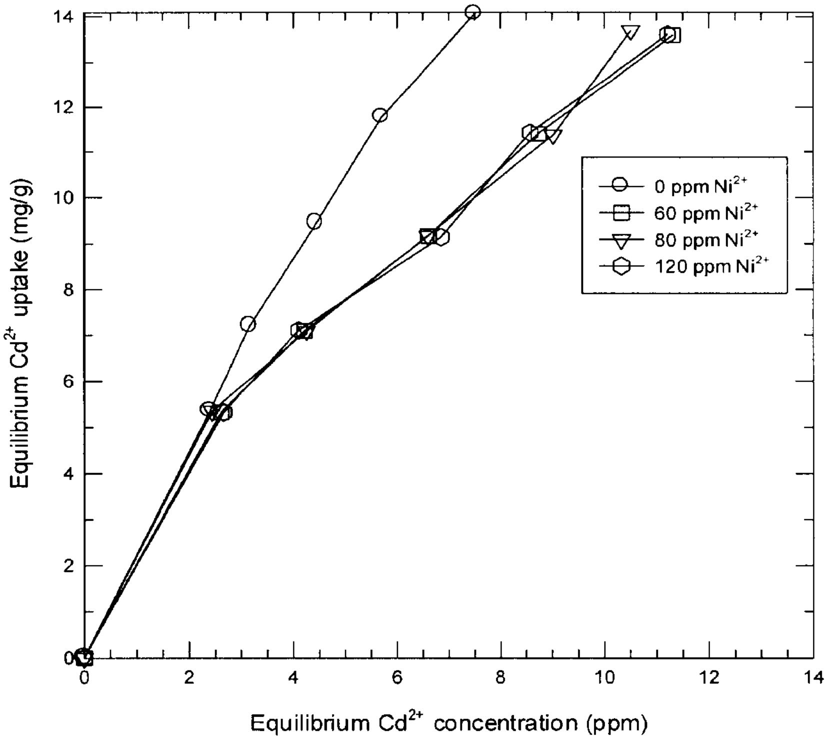


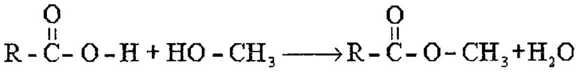
Figure 2. Effect of the presence of Ni^{2+} on the adsorption of Cd^{2+} in (Cd^{2+}–Ni^{2+}) binary system. Initial Ni^{2+} concentration = 0–120 ppm, and initial Cd^{2+} concentration = 40–120 ppm.

Table 2. Investigation of ion exchange mechanism. Initial metal ion concentration = 100 ppm, SMW concentration = 8 mg/mL in the case of Ni^{2+} and Cd^{2+}.

		Cation released (mEq/L)			
Metal	Metal bound (mEq/L)	Ca^{2+}	K^+	H^+	($R_{b/r}$)
Ni^{2+}	2.1	0.24	0.87	0	1.89
Cd^{2+}	1.6	0.12	0.026	0	11.00

was investigated by monitoring the release of Ca^{2+}, K^+, and H^+ during the adsorption process. The amounts of the released cations were compared with those in a control sample, which consisted of SMW and distilled water. The difference is due to the binding of heavy metals to SMW. The equivalent ratio ($R_{b/r}$), defined as the ratio of metal bound to cation released, is next calculated. If this ratio is greater than unity, then the ion exchange mechanism is not the only mechanism in the adsorption process. Table 2 shows the amount of metal ions bound and the amount of released cations due to metal binding along with the calculated $R_{b/r}$. As can be seen from this table, the amount of bound metals for the two metals is greater than the amount of released cations, which resulted in $R_{b/r}$ values greater than 1. This implies that the ion exchange mechanism is not the only mechanism in the sorption process.

Among the functional groups that exist on the surface of SMW that may be responsible for the ion exchange and complexation, the carboxyl group was examined in this study. The contribution of carboxyl groups in the adsorption process was studied by blocking the carboxyl groups on the SMW. This was done using the method proposed by Gardea-Torresdey et al.[21] According to this method, the carboxyl groups are chemically blocked by methanol esterification according to the following reaction:



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-H + HO-CH_3 \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_3 + H_2O$$

Therefore, if the interaction with carboxyl groups contributes to the binding of heavy metals on SMW, blocking of the carboxyl groups would cause a reduction in the metal binding. Figure 3 shows the effect of esterification on the adsorption of Ni^{2+}, and Cd^{2+}. As can be noticed, the blocking of carboxyl groups reduces the removal of metal ions, which implies that carboxyl groups contribute to the binding of heavy metals on SMW.

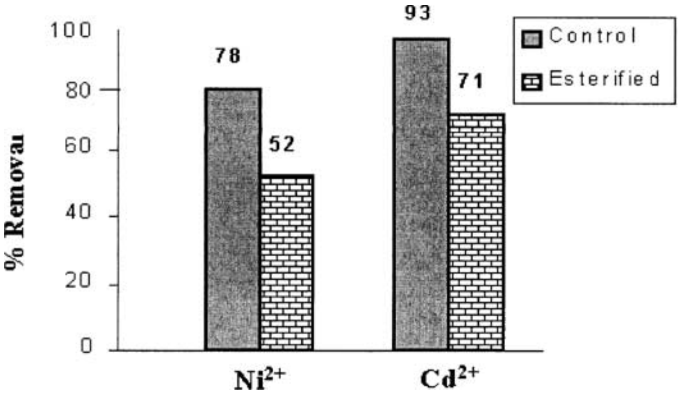


Figure 3. Effect of blocking the carboxyl groups on the percentage removal of metal ions by SMW. Initial metal ion concentration = 100 ppm, SMW concentration = 8 mg/mL.

However, this reduction was not 100%, implying that the carboxyl groups are the only groups responsible in the adsorption process.

Prediction of Binary Isotherms Using Single Adsorption Data

The experimental measurement of multicomponent adsorption isotherms is time consuming because of the large number of variables involved. Thus, the problem of predicting binary equilibrium isotherm from single component adsorption data has attracted a lot attention. Several isotherms have been proposed to describe the competitive adsorption. Most of these isotherms are based on the single component isotherm parameters without any information other than experimental competitive data. Other competitive isotherms are based on single component isotherm parameters and correction factors extracted from the experimental competitive data.

The Langmuir isotherm can be extended for multicomponent systems to give the following form[22]:

$$q_{e,i} = \frac{Q_{o,i} b_i C_{e,i}}{1 + \sum_{k=1}^{N} b_k C_{e,k}} \tag{1}$$

Where $C_{e,i}$ is the equilibrium concentration of the component i in the multicomponent solution (mg/L), $q_{e,i}$ is the equilibrium uptake of the component i (mg/g), and $Q_{\mathrm{o},i}$ and b_i are the single component Langmuir parameters for the component i. For each component in the binary system, Eq. (1) can be written as:

$$q_{e,1} = \frac{Q_{o,1} b_1 C_{e,1}}{1 + b_1 C_{e,1} + b_2 C_{e,2}} \tag{2}$$

$$q_{e,2} = \frac{Q_{o,2} b_2 C_{e,2}}{1 + b_1 C_{e,1} + b_2 C_{e,2}} \tag{3}$$

This model (often called extended Langmuir model) is applicable when each single component obeys the Langmuir model in a single component system.[22] A modified Langmuir equation was proposed to account for competition in extended Langmuir equation.[22] An additional term was added into Eq. (2):

$$q_{e,1} = \frac{(Q_{o,1} - Q_{o,2}) b_1 C_{e,1}}{1 + b_1 C_{e,1}} + \frac{Q_{o,1} b_1 C_{e,1}}{1 + b_1 C_{e,1} + b_2 C_{e,2}} \tag{4}$$

The additional term in Eq. (4) is the Langmuir expression for the number of molecules of component 1 that is adsorbed without competition on the adsorbent surface area, which is proportional to $(q_{o,1} - q_{o,2})$. The second term represents the number of molecules of component 1 that is adsorbed on the surface area in competition with component 2, which is proportional to $q_{o,1}$. The number of molecules of component 2 that is adsorbed on the surface area in competition with component 1 is proportional to $Q_{\mathrm{m},2}$, which can be calculated from Eq. (3).

The competitive Redlich–Peterson and Sips[23] models related to the individual isotherm parameters are given by Eqs. (5) and (6), respectively.

$$q_{e,i} = \frac{K_{R,i} b_{R,i} C_{e,i}}{1 + \sum_{k=1}^{N} b_{R,k} (C_{e,k})^{n_{R,i}}} \tag{5}$$

$$q_{e,i} = \frac{Q_{m,i} (b_{s,i} C_{e,i})^{\frac{1}{n_{s,i}}}}{1 + \sum_{k=1}^{N} (b_{s,k} C_{e,k})^{\frac{1}{n_{s,k}}}} \tag{6}$$

where $K_{\mathrm{R},i}$, $\mathrm{b}_{\mathrm{R},i}$, and $\mathrm{n}_{\mathrm{R},i}$ are the Redlich–Peterson single component parameters for component i, and $\mathrm{Q}_{\mathrm{m},i}$, $\mathrm{b}_{\mathrm{S},i}$, and $\mathrm{n}_{\mathrm{S},i}$ are the sips single component parameters for component i.

In this study, the adsorption isotherms of single metals (i.e., single nickel and cadmium) were used to predict the binary adsorption data using the single metal adsorption parameters listed in Table 3.[18,19] Metal ion uptakes were

Table 3. Model parameters of adsorption of single metals on SMW.[18,19]

Model	Parameter	Ni^{2+}	Cr^{2+}
Langmuir	Q_o (mmol/g)	0.290	0.438
	b (L/mmol)	2.13	6.02
Sips	Q_m (mmol/g)	0.24	0.61
	b_s (L/mmol)	3.17	3.56
	n_s	0.77	1.07
Redlich–Peterson	K_R (L/g)	0.49	2.00
	b_R (L/mmol)	1.53	5.1
	n_R	1.41	0.58

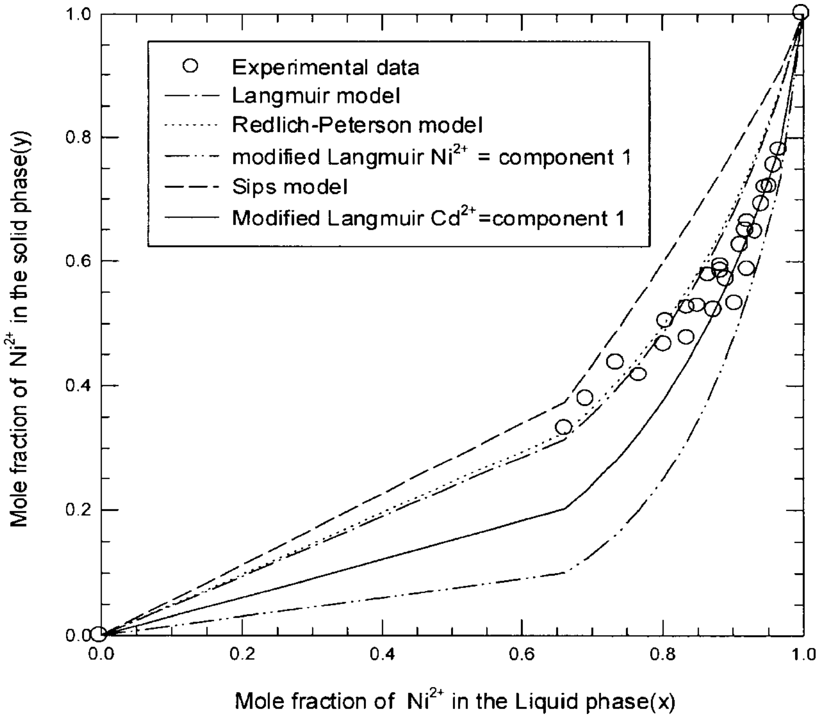


Figure 4. Prediction of binary adsorption isotherms from single component adsorption data for (Ni^{2+}–Cd^{2+}) system. Initial Ni^{2+} concentration = 40–120 ppm, and initial Cd^{2+} concentration = 40–120 ppm.

Table 4. RMSD for the predicted mole fraction for the Cd^{2+}–Ni^{2+} binary system.

Model	RMSD
Langmuir	0.015
Redlich–Peteson	0.016
Modified Langmuir	0.031 (Ni^{2+} = component 1); 0.011 (Cd^{2+} = component 1)
Sips	0.030

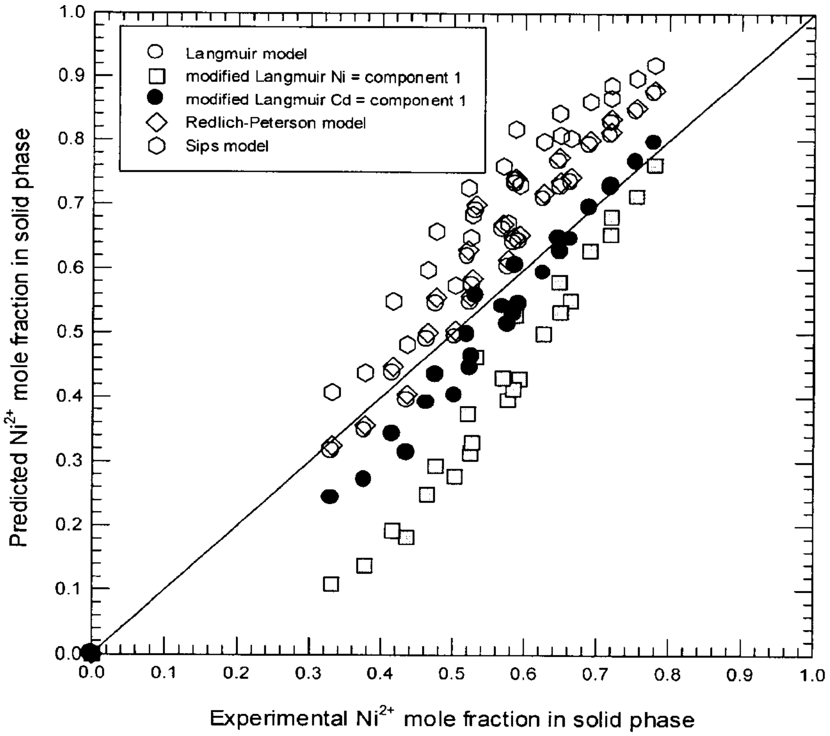


Figure 5. Comparison between experimental and model-predicted nickel mole fraction in solid phase (y) in (Ni^{2+}–Cd^{2+}) system. Initial Ni^{2+} concentration = 40–120 ppm, and initial Cd^{2+} concentration = 40–120 ppm.

calculated using the multiadsorption isotherm models previously described. The calculated uptakes were compared with the experimental ones. Since more than one metal was present in the liquid or solid phases, mole fraction in the liquid phase and in solid phase, rather than uptake and concentration, were used to plot the results. Figure 4 shows the relationship between equilibrium mole fraction in the solid phase and that in the liquid phase for ($Ni^{2+}-Cd^{2+}$) system. Root-mean-square-deviation (RMSD) relating the measured and the predicted uptakes was used to evaluate and compare the prediction of the different models. The corresponding RMSD values are presented in Table 4. As can be noticed from these results, the Langmuir, modified Langmuir, and Redlich–Peterson models gave very good predictions of the binary data. Notice that the Modified Langmuir model showed poor prediction when nickel was assumed to be component 1, as can be seen from Fig. 4 and RMSD values. When cadmium was assumed as component 1, the modified Langmuir model showed the best prediction, as shown in Figs. 4 and 5, which implies that cadmium has higher a affinity than nickel.

CONCLUSION

Competitive adsorption of nickel and cadmium ions in sheep manure waste was investigated in this study. The experimental results showed that when more than one metal coexisted in the solution, they would compete with each other for the available binding ligands. Metals with higher affinity to the surface ligands will bind and attach easier and more to the surface. It was found that both cadmium and nickel affect the uptake of each other, but the presence of nickel was found to depress significantly cadmium uptake.

The validity of predicting the $Ni^{2+}-Cd^{2+}$ adsorption isotherm using the data from a single metal adsorption isotherm was assessed using different isotherm models; extended Langmuir, extended Redlich–Peterson, extended Sip, and modified Langmuir isotherm models. The Langmuir, modified Langmuir, and Redlich–Peterson models predicted the equilibrium data of adsorption of the binary $Ni^{2+}-Cd^{2+}$ ion SMW very well when cadmium was assumed to be component 1.

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