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Removal of Cu(II) and Zn(II) from industrial wastewater by acid-activated montmorillonite-illite type of clay

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ABSTRACT

An acid-activated montmorillonite-illite type of clay collected from the Gulbarga region of Karnataka, India was examined for removing copper and zinc ions from industrial wastewater containing Cu(II), Zn(II) and minor amounts of Pb(II). Langmuir, Freundlich, Brunauer-Emmett-Teller (BET), and competitive Langmuir (two competing ions) isotherms were fitted to experimental data and the goodness of their fit for adsorption was compared. The shapes of isotherms obtained indicated multilayer adsorption of Cu(II) and monolayer adsorption of Zn(II) on the acid-activated clay. Competitive adsorption was found to be significant due to the presence of Cu(II) in the wastewater.

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1. Introduction

Heavy metals accumulate in the food chain and persist in nature due to their discharge by many industrial activities. There are many treatment processes that can be used for the removal of metal ions from wastewater and the cost of operation plays an important role for determining which one is to be applied. As a result, in the last few decades, different adsorbents for the treatment of heavy metal contamination have been investigated. Despite the fact that single toxic metallic species rarely exist in wastewater, they are mostly analyzed in a single model system, possibly for the reason of better knowledge of adsorption phenomena. Some researchers investigated the adsorption from binary or multi-metal systems [1–4]. Besides heavy metal ions, industrial metal-bearing wastewater also contains other materials, such as supplementary cations, chelating agents, and other organic materials. All these can produce three possible types of behavior:

synergism (the interaction of two different ions to produce an effect greater than the sum of their individual effects), antagonism (two or more different ions in combination have an overall effect which is less than the sum of their individual effects) and non-interaction. Thus, any study of adsorption characteristics of adsorbents in single metal solutions may only be considered as preliminary. Also, the literature is still scarce to cover the problem of multi-metal adsorption from real wastewaters. Some of the work available in the literature on multi-metal adsorption is cited in references [5–12].

In this work, isotherm studies on an acid-activated montmorillonite-illite clay [MIC(AA)] available in the Gulbarga region of Karnataka state, India, in removing heavy metal ions from industrial wastewater were examined.

Four isotherm models, viz: Freundlich [13], Langmuir [14], Brunauer-Emmett-Teller (BET) [15], and competitive Langmuir [16] (two competing ions) were applied to describe adsorption in this study. For modelling heavy metal adsorption from wastewater, these models have been previously applied by some researchers [1,17]. The isotherm parameters and correlation coefficients (R) were computed from the linearized forms of these isotherm equations.

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Nomenclature

C_0	Initial metal ion concentration (mg/L)
C_e	Residual metal ion concentration (mg/L)
m	Mass of adsorbent (g)
V	Solution volume (L)
q_e	Equilibrium metal uptake by the adsorbent (mg/g)
η	Adsorption efficiency
BET	Brunauer-Emmett-Teller
MIC	Montmorillonite-illite clay
MIC(AA)	Montmorillonite-illite clay (acid activated)
FTIR	Fourier transform infrared
R	Correlation coefficient

Langmuir (monolayer) and Freundlich (multilayer) models were applied since they are simple and widely used for adsorption studies in aqueous solutions. The BET model represents an extension of the Langmuir model for multilayer adsorption. It is based on the assumption that each adsorbate in the first adsorbed layer serves as an adsorption site for the second layer, and so on. The difficulties in describing the adsorption of metal ions from wastewater resulted from the presence of several different components, causing interference and competition on adsorption sites. Therefore, it was necessary to use the competitive Langmuir model for two competing ions, in order to express the relationships between the quantity of the first component adsorbed and the concentration of the second component. All isotherms were fitted to experimental data, and the goodness of their fit was compared.

2. Materials and methods

2.1. Clay adsorbent

A sample of 20 g of raw clay montmorillonite-illite clay (MIC) in the particle size range 425 μm to 212 μm was mixed with 400 mL of H_2SO_4 solution which had 45% of H_2SO_4 by mass of the clay. The acid activation of the clay was performed by heating for six hours in a shaking water bath at 97 °C with reflux condensing of the vapors [18]. The activated clay sample was then washed several times with distilled water to remove sulfate ions. The sample was then dried in an air oven for 24 hours at 105 °C and stored in air tight polythene sachets. The acid-activated clay fraction in the size range 212 μm to 102 μm was used for experimentation.

2.2. Wastewater

Multi-metal ions containing industrial wastewater was collected from an electroplating factory in Bangalore, Karnataka, India. It was filtered through a qualitative filter paper and stored at 5 °C for further use. Chemical oxygen demand (COD) in wastewater was determined by means of

dichromate method [19] and biochemical oxygen demand (BOD) by standard method [20].

2.3. Batch adsorption studies

Batch adsorption experiments were carried out at constant room temperature of 38 °C by adding different amounts of adsorbent to flasks containing wastewater, without adjusting pH. The flasks were shaken on a laboratory shaker for three hours. This contact time was sufficient to achieve equilibrium in the system for all heavy metal ions present in wastewater [21]. After that, the adsorbent was separated by vacuum filtration through a Gooch G3 crucible and the filtrate was analyzed for metal ions.

The concentrations of heavy metal ions before and after adsorption experiments were determined using an inductively coupled plasma atomic emission spectrometer (ICPAES), Thermo Electron IRIS INTREPID II XSP DUO instrument. Adsorption efficiency (η) was expressed as a percentage of adsorbed metal compared to initial metal concentration as:

$$\eta = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad (1)$$

The amount of metal ions adsorbed was calculated as:

$$q_e = \frac{(C_0 - C_e)}{m/V} \quad (2)$$

where, C_0 and C_e are the initial and residual concentrations of metal ion, respectively, m is the adsorbent dosage and V is the solution volume. q_e is the equilibrium metal uptake by the adsorbent.

3. Results and discussion

3.1. Characteristics of adsorbent and wastewater

Acid treatment of clays creates new pores resulting in an increase of surface acidity through the replacement of cations, like Al^{3+} , Fe^{3+} and Ca^{2+} from the structure with H^+ [22]. During clay activation with mineral acids, the acid first dissolves part of Al_2O_3 as well as CaO and MgO from the lattice, which leads to opening of the crystal lattice and an increase in internal surface area. Then, there is gradual exchange of the Ca and Mg ions located at the surface of the crystal against hydrogen ions from the mineral acid. Acid-activated clay is almost saturated with H^+ ions and exhibits acidic character and better adsorption property.

X-ray fluorescence instrument (ARL/XRF – 8600) was used to identify the oxides composition of the MIC and MIC(AA) (Table 1). The physical specifications of the activated clay adsorbents used in the study are also given in Table 1. Major oxides in the adsorbent were SiO_2 , Al_2O_3 , Fe_2O_3 and CaO . Properties of the adsorbents, such as specific gravity, pH and loss on ignition, were determined by standard procedures [23].

Mineral phase analysis of the raw and acid-activated clay was carried out in a Bruker AXS D8 powder XRD instrument. Some of the calcium, potassium and magne-

Table 1
Oxides composition and specifications of the raw and acid-activated clay.

Oxides	Weight (%)	
	MIC	MIC(AA)
SiO ₂	48.523	53.996
Al ₂ O ₃	9.682	8.937
Fe ₂ O ₃	18.809	14.093
CaO	17.042	16.751
MgO	3.971	2.863
K ₂ O	1.768	2.265
Na ₂ O	0.139	0.140
SO ₃	0.065	0.955
Specification		
Particle size range	212 μm to 106 μm	212 μm to 106 μm
Average particle size	~160 μm	~160 μm
Specific gravity	2.4	1.78
pH	8	4.15
Langmuir surface area	156 m ² /g	251 m ² /g
Loss on ignition	11.1%	6.94%

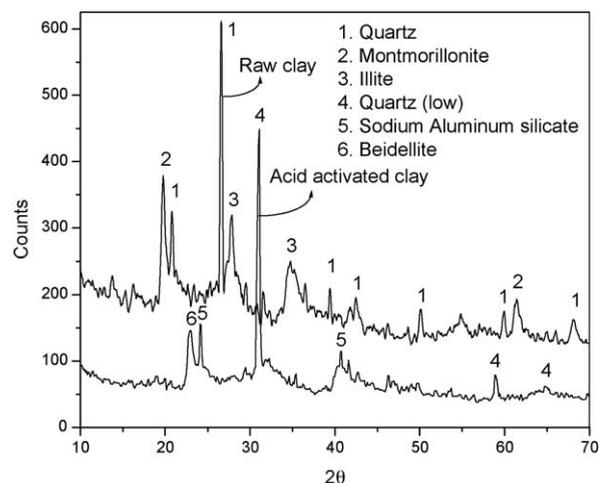


Fig. 1. XRD of raw and acid-activated clays.

sium were removed from the clay as their corresponding sulfates during acid activation, which led to the disappearance of the montmorillonite and illite phases in raw clay. Also, there was inversion of quartz to quartz (low) due to acid activation. The XRD patterns are shown in Fig. 1 and the mineral phase compositions are given in Table 2.

The characteristics of the wastewater after filtration are presented in Table 3. FTIR spectrum of the wastewater (obtained with Thermo Nicolet Avatar 370 instrument),

Table 2
XRD phase analysis of raw and acid-activated clay.

Adsorbent	Compounds	Chemical formula
MIC	Quartz	SiO ₂
	Montmorillonite	(Na,Ca) _{0.3} (Al,Mg) ₂ Si ₄ O ₁₀ (OH) ₂ .xH ₂ O
	Illite	KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂
MIC(AA)	Quartz (low)	SiO ₂
	Sodium Aluminum Silicate	Na ₈ Al ₄ Si ₄ O ₁₈
	Beidellite	Na _{0.3} Al ₂ (Si,Al) ₄ O ₁₀ (OH) ₂ .2H ₂ O

Table 3
Characteristics of wastewater.

Parameter	Value
pH	2.40
COD (mg O ₂ /L)	690.00
BOD (mg O ₂ /L)	275.00
Cu (mg/L)	280.32
Zn (mg/L)	382.72
Pb (mg/L)	17.00
Total dissolved solids (mg/L)	425.00

COD: chemical oxygen demand; BOD: biochemical oxygen demand.

showing the significant absorption bands with the respective assignments, is given in Fig. 2.

3.2. Isotherm analysis

The acid-activated clay was tested for simultaneous adsorption of Cu(II) and Zn(II) from the industrial wastewater. The wastewater was filtered and diluted (4×) so as to reduce the Pb(II) concentration to a low level. Batch adsorption studies were performed with the diluted wastewater at room temperature. Fig. 3 shows the adsorption efficiencies achieved. As the solid/liquid ratio (m/V) was increased, the adsorption efficiency increased for Zn(II) as expected. However, it was observed that Zn(II) was a competing ion for Cu(II). Fig. 4 shows the adsorption isotherms for Cu(II) and Zn(II) on the acid-activated clay. The shapes of the adsorption isotherms indicated that the adsorption of two or more metals from wastewater was much complex than mono-metal adsorption. Investigations of adsorption from binary metal systems show different curves of adsorption plots influenced by competition phenomena [1]. The shapes of the adsorption isotherms obtained indicated that the adsorption from wastewater was multilayer. Table 4 gives the isotherm equations and Table 5 gives the values of the isotherm parameters and correlation coefficient (R) obtained by linear fitting using Origin 6[®] software.

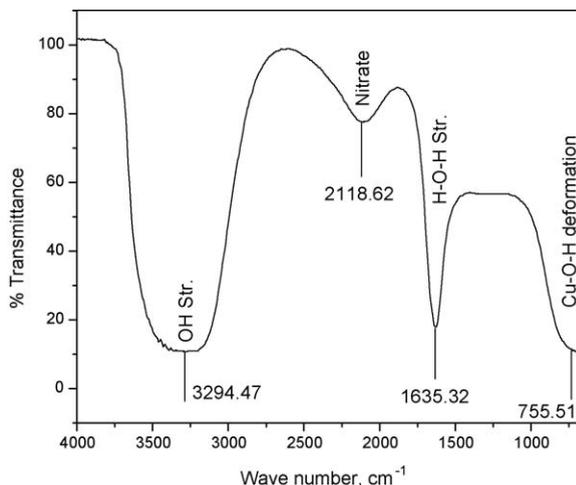


Fig. 2. FTIR of wastewater.

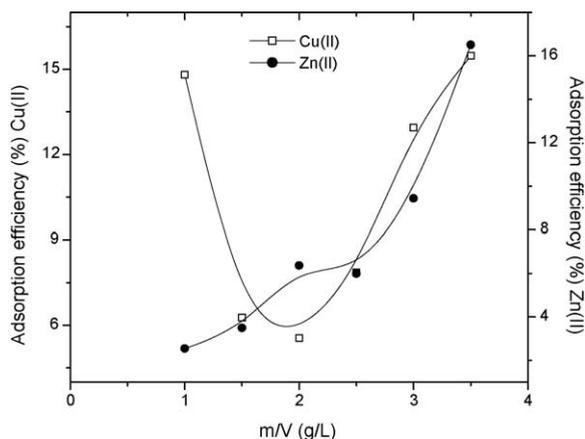


Fig. 3. Adsorption efficiencies of Cu(II) and Zn(II) on acid-activated clay at 38 °C.

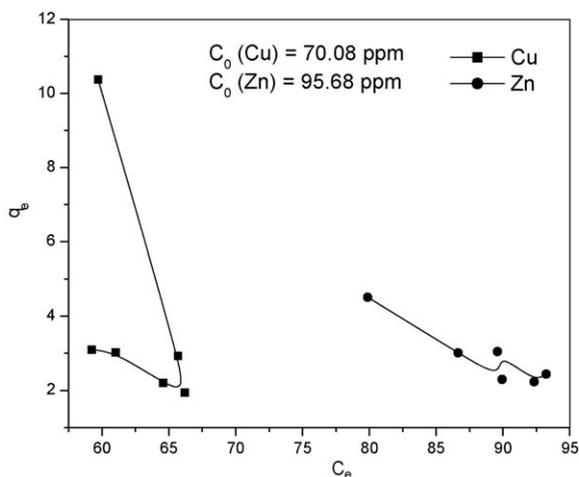


Fig. 4. Adsorption isotherms at 38 °C, shaking time three hours.

Some researchers [1,2,10] observed that competitive adsorption was significant in binary or multi-metal systems when copper ions were present. This is a consequence of its paramagnetic nature and high electronegativity, and the pH values corresponding to bonding of aqua-hydroxocomplexes [24]. It was also observed that the copper and zinc ions have a synergistic effect. Hence, it is apparent that there is more than one factor playing important role in the adsorption process. Moreover, these factors may interact with each other and the conclusions extracted from the experiments with real wastewater are valid only for certain conditions and do not represent a general rule.

The Freundlich isotherm showed an inverse fit to the linearized equilibrium data for the adsorption of both Cu(II) and Zn(II) on the acid-activated clay due to the competing nature of the adsorption process. The linearized equilibrium data for the adsorption of both Cu(II) and Zn(II) on the acid-activated clay gave satisfactory fit to Langmuir, BET and competitive Langmuir models. The best fit, however, for Cu(II) was provided by BET model, and for Zn(II) by

Table 4
Isotherm models.

Model	Equation	Parameters
Freundlich	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	K_F, n
Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$	q_m, K_L
BET	$\frac{C_e}{q_e(C_0 - C_e)} = \frac{1}{q_m k} + \frac{(k-1)}{q_m k} \left[\frac{C_e}{C_0} \right]$	q_m, k
Competitive Langmuir	$q_{i,eq} = \frac{q_{m,i} K_i C_{i,eq}}{1 + K_i C_{i,eq} + K_j C_{j,eq}}$	$q_{m,i}, K_i, K_j$

Table 5
Parameter values and correlation coefficients of isotherm models.

Isotherm model	Parameters	Values for the adsorption of	
		Cu(II)	Zn(II)
Freundlich	K_F	3.46E14	9.43E08
	n	-0.1281	-0.2284
	R	-0.6496	-0.9320
Langmuir	q_m	0.4076	0.5844
	K_L	-0.0186	-0.0144
	R	0.7843	0.9302
BET	q_m	5.5E-06	1.6E-06
	k	-3397.6	-7583.7
	R	0.9142	0.8560
Competitive Langmuir	q_m	0.2573	0.4168
	K	-0.0720	-0.0584
	R	0.8325	0.8882

Langmuir model. Hence, it was confirmed that the Cu(II) adsorption from wastewater on the clay was multilayer, but Zn(II) adsorption was, probably, monolayer.

However, despite numerous investigations, the fundamental aspects of cation uptake from wastewaters are not well understood and conclusions about the mechanisms are divergent [9,25].

4. Conclusions

In this study, the ability of an acid-activated montmorillonite-illite type of clay to bind Cu(II) and Zn(II) from industrial wastewater was investigated. Results obtained were modelled using four adsorption models: Langmuir, Freundlich, BET and competitive Langmuir and the goodness of their fit was compared. Based on the results, it can be concluded that the adsorption of Cu(II) from the wastewater on the adsorbent was multilayer and that of Zn(II) was monolayer.

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