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Zinc removal from aqueous solution using an industrial by-product phosphogypsum

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Abstract

The removal of zinc(II) ions from aqueous medium by phosphogypsum was examined. The removal capacity of phosphogypsum for zinc(II) ions was studied as a function of solution pH, contact time, adsorbent dosage and adsorbate concentration. Phosphogypsum was pre-conditioned with lime milk before the adsorption studies. The maximum adsorption of the zinc(II) ions on the phosphogypsum was observed at the pH values between 9.0 and 10.0. It was observed that the adsorption equilibrium was reached in 40 min and the adsorption data fitted well to Freundlich model. The adsorption capacity of phosphogypsum for zinc(II) ions was determined to be 2.57 mg g^{-1}. The results showed that the phoshogypsum is a suitable adsorbent for the removal of zinc(II) ions from aqueous solutions.

Keywords: Adsorption; Batch; Isotherm; Phosphogypsum; Zinc

1. Introduction

The United States Environmental Protection Agency (USEPA) prepared a list of organic and inorganic pollutants, which are found in wastewater and constitute serious health hazards, in 1978. Zinc is one of the 13 important toxic metals cited in this list [1]. It is widely available in industrial effluents involved in acid mine drainage, galvanizing plants, natural ores and municipal wastewater treatment plants [2]. High releasing of zinc (Zn) into environment is also from non-point sources of pollution due to agricultural activities, sediment remobilization or entrainment, groundwater intrusion or from a combination of these sources [3].

In recent years, various removal methods have been developed for the treatment of heavy metal containing wastewaters. Chemical precipitation, solvent extraction, reverse osmosis, ion exchange, evaporation, fixation/solidification, filtration, adsorption, oxidation, reduction, dialysis/electrodialysis, etc. are the most widely employed techniques for the removal of metal ions from industrial wastewaters. In spite of their common usage for the removal of heavy metals from water and wastewater, they have some disadvantages, e.g. they may be expensive, ineffective for low metal concentrations (around 1–100 mg L^{-1}), produce toxic sludge or other waste products that require disposal, and require the uses of high reagent and energy [4–6].

Among these methods, adsorption has especially been applied as an efficient method for removal of present heavy metals at low concentrations. Nowadays, activated carbon is also used as a common adsorbent for the metal removal from water and wastewater [7].

Although a variety of activated carbons are available commercially, very few of them are selective for heavy metals. Also, they are very costly [7]. Therefore, the use of new and inexpensive adsorbents for the removal of metals from wastewaters seems necessary. In recent years, several low-cost and nonconventional natural materials, industrial by-products, and agricultural wastes have been examined for the removal of metal ions from water systems [8–20]. The results obtained showed that these adsorbents were employed efficiently in the removal of Zn(II) ions from the aqueous solutions.

We have recently reported a nonconventional adsorbent which is phosphogypsum, a waste material of the dihydrate wet phosphoric acid process from fertilizer plant, for the removal of lead ions from synthetic wastewater [21,22].

In the present work, the adsorption of Zn(II) ions by phosphogypsum was studied by investigating the influence of different

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process variables on Zn(II) uptake, such as pH, contact time, adsorbent dosage and adsorbate concentration. The adsorption isotherms were obtained and modelled according to both Langmuir and Freundlich models.

To our knowledge, no papers dealing with Zn(II) retention from aqueous solutions by phosphogypsum have been published.

2. Materials and methods

Phosphogypsum was obtained from TÜGSAŞ Fertilizer Plant in Samsun, Turkey and its fraction with particle size of 65 mesh was used in the removal of Zn(II) ions. Before the adsorption studies, phosphogypsum was pre-conditioned with lime milk as described by Ölmez and Yılmaz [23].

Some physical and chemical characteristics of that untreated phosphogypsum have already been reported by Ölmez and Yılmaz [23] and Balkaya and Cesur [22].

Adsorption experiments were carried out in 250 mL capacity Erlenmeyer flasks. Given amounts of lime-preconditioned phosphogypsum were added to 100 mL of Zn(II) solutions in Erlenmeyer flasks and shaked at 200 rpm and room temperature (Clifton NE5 28D Model Shaking Water Bath). The solutions were separated from reaction mixtures using a centrifuge and the concentrations of Zn(II) ions in the supernatant were determined by an atomic adsorption spectrophotometer (ATI UNICAM 929 Model Flame AAS). The pH of each solution was adjusted to the desired value with HNO_3 or NaOH before the contact of adsorbent with metal ion solution. Each experiment was performed twice under identical conditions. The reproducibility, of the measurements was generally within 5%.

The amount of Zn(II) adsorbed on the phosphogypsum ($\mathrm{mg\,g^{-1}}$) was calculated by using the equation given below:

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

where C_o and C_e are the initial and equilibrium concentrations of Zn(II) ion in the solution, respectively ($\mathrm{mg\,L^{-1}}$), V is the volume of solution (L) and W is the weight of the adsorbent (g).

3. Results and discussion

3.1. Influence of process variables

3.1.1. Effect of pH

The effect of pH on Zn(II) adsorption by phosphogypsum was given in Fig. 1. It can be seen from this figure that the minimum Zn(II) adsorption occurs in the pH range of 2.5–7.0. The low Zn(II) adsorption at low pH may be due to high acidity of solution, and the competition between the H^+ and Zn(II) ions for the adsorption. The H^+ ions are preferentially adsorbed over adsorbent surface. Thus, it hinders the positively charged metal ions to reach to the binding sites of the adsorbent. It is known that the solution pH affect both the solution chemistry and the surface binding sites of the phosphogypsum [16]. Similarly, an increase in Zn(II) uptake with the increase in solution pH was reported by Ricou et al. [24] for fly ash, Annadurai et al. [16] for residues of banana and orange peels, Mohan and Singh [7] for bagasse carbon, Wang et al. [17] for Fe_2O_3, Fe_3O_4, FeS, steel wool, Mg pellets, Cu pellets, Al pellets, Fe pellets and coal, Yan and Viraraghavan [25] for fungus *Mucor rouxii*, Zouboulis et al. [26] for dead fungal biomass immobilized by polyacrylonitrile, Weng and Huang [27] for fly ash and Kandah [28] for low grade phosphate.

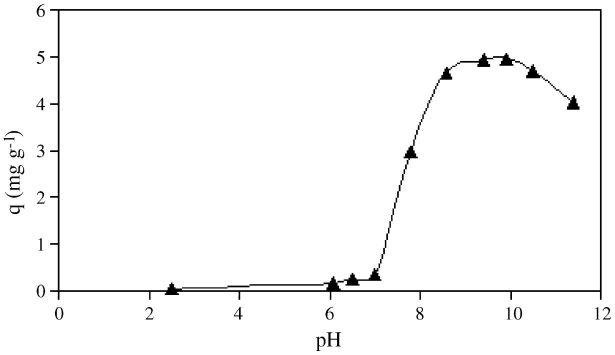

Fig. 1. Effect of initial pH (initial concentration of Zn(II), $50\ \mathrm{mg\,L^{-1}}$; phosphogypsum dosage, $10\ \mathrm{g\,L^{-1}}$; contact time, 2 h).

Zn(II) adsorption by phosphogypsum increased with the increase in pH and reached a maximum in the pH range of 9.0–10.0. Zouboulis et al. [26] have reported that maximum removal of Zn(II) ions by dead fungal biomass immobilized by polyacrylonitrile was achieved at pH between 9.0 and 10.0. These findings are in good agreement with that of our work. Also, Lu and Chiu [29] have revealed that the adsorption of Zn(II) onto carbon nanotubes reached a maximum in the range of 8–11.

It is known that the dominant zinc species is Zn(II) for $\mathrm{pH} < 8$ and the Zn(II) removal is mainly acomplished by adsorption reaction. In the range of 8–11, the main species are $Zn(OH)^+$, $Zn(OH)_2{}^0$ and $Zn(OH)_3{}^-$ and thus the removal of Zn is possibly accomplished by simultaneous precipitation of $Zn(OH)_{2(s)}$ and adsorption of $Zn(OH)^+$ and $Zn(OH)_3{}^-$. At a pH of 12, the predominant zinc species are the negative species $Zn(OH)_3{}^-$ and $Zn(OH)_4{}^{2-}$ [30]. Therefore, it can be said that the decrease in Zn removal that took place at a pH of 12 (Fig. 1) can be attributed in part to competition among OH^-, $Zn(OH)_3{}^-$ and $Zn(OH)_4{}^{2-}$ ions on the same sites [29].

3.1.2. Effect of contact time

Fig. 2 shows the effect of contact time on the removal of Zn(II) ions from aqueous solutions by phosphogypsum. The metal uptake is rapid in the first 10 min of contact period. Beyond the 45 min contact time, the amount of Zn(II) adsorbed on the phosphogypsum remains constant as shown in Fig. 2. These data indicate that the equilibrium is attained after 40 min.

3.1.3. Effect of adsorbent dosage

Fig. 3a and b shows the effect of adsorbent dosage on Zn(II) adsorption. As it can be seen from Fig. 3a that while the removal percentage of Zn(II) increased with the increase in adsorbent dosage, but the amount of Zn(II) adsorbed by unit weight of the adsorbent decreased (Fig. 3b). It can be said that the decrease in

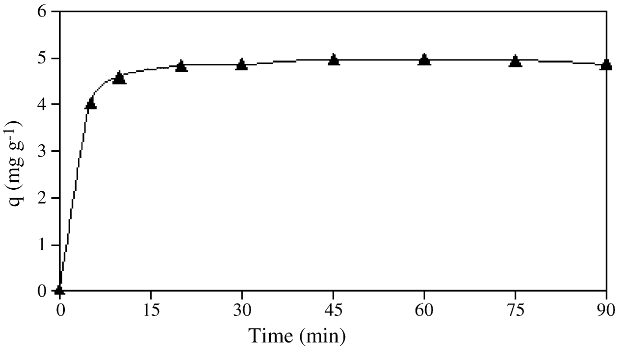

Fig. 2. Effect of initial contact time (initial concentration of Zn(II), 50 mg L^{-1}; phosphogypsum dosage, 10 g L^{-1}; pH 9.5).

the adsorbed amount with the increase in adsorbent dosage may result from the electrostatic interactions, interference between binding sites, and reduced mixing at higher adsorbent densities [31–33]. This finding agrees with those of Gong et al. [34] for Cr(VI) removal by intact and pre-treated *Spirulina maxima* biomass, Yabe and de Oliveira [35] for metal removal by sequential adsorbent treatment (using solid adsorbents such as sand, silika, coal and alumina), Montanher et al. [33] for Zn(II) removal by rice bran, and Kwon et al. [36] for Zn(II) removal by scoria.

3.1.4. *Effect of adsorbate concentration*

The effect of initial adsorbate concentration on the adsorption was investigated by varying the initial concentration of Zn(II) between 0.1 and 100.0 mg L^{-1}. The experimental data were illustrated in Fig. 4. It was observed that Zn(II) adsorption increased linearly with the increase in Zn(II) concentration for the concentration range of 0.1–100.0 mg L^{-1}. This increase may result from an increase in electrostatic interactions, involving sites of progressively lower affinity for Zn(II) ions [36,37].

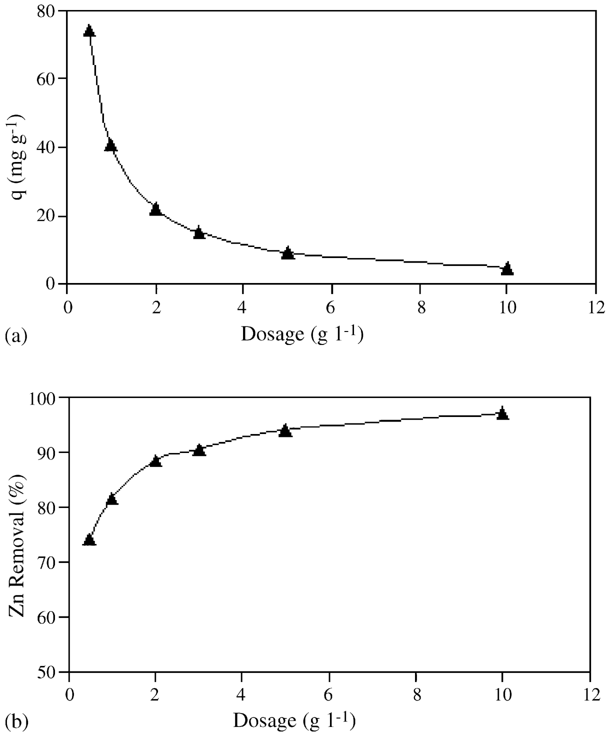

Fig. 3. Effect of phosphogypsum dosage: (a) Zn(II) removal (%) and (b) adsorbed Zn(II) (mg g^{-1}) (initial concentration of Zn(II), 50 mg L^{-1}; contact time, 45 min; pH 9.5).

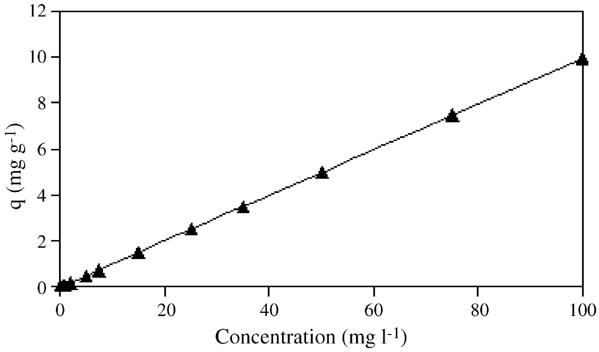

Fig. 4. Effect of initial Zn(II) concentration (phosphogypsum dosage, 10 g L^{-1}; contact time, 45 min; pH 9.5).

3.2. *Comparative study*

In this work, in order to compare the effect of type of the adsorbent on the Zn(II) removal, the adsorption experiments were performed by lime, raw phosphogypsum, and lime-preconditioned phosphogypsum, and the data obtained were presented in Table 1. Removal percentage of Zn(II) by lime-preconditioned phosphogypsum was almost equal to that of Zn(II) by using raw phosphogypsum. Removal percentage of Zn(II) by equal amount of lime with that of lime adsorbed by the phosphogypsum during precondition was 29.5%. The decrease in Zn(II) removal by lime is probably resulting from the increase in pH due to basic nature of lime. As can be seen from Fig. 1, Zn(II) removal decreased remarkably with the increase in pH of adsorption media at pH higher than 10. In contrast, an effective Zn(II) removal was achieved by the use of lime-preconditioned phosphogypsum as adsorbent. Also, comparative studies indicated that the removal of Zn(II) by phosphogypsum in alkaline pH may be mainly accomplished by adsorption reaction.

It can be said that the precondition of phosphogypsum by lime leads to the formation of an adsorbent with synergistic effect for Zn(II) removal compared to the raw phosphogypsum. In addition, the precondition of phosphogypsum by lime

Table 1
The removal percentage of Zn(II) from aqueous solution using lime, raw and lime-preconditioned phosphogypsum (Zn(II), 50 mg L^{-1}; pH 10.0; contact time, 45 min)

Materials	Removal percentage of Zn(II) (%)
Lime (0.28 g L^{-1})	26.5
Raw (unconditioned) phosphogypsum (10 g L^{-1})	96.4
Lime-preconditioned phosphogypsum (10 g L^{-1})	97.2

milk neutralises the water-soluble impurities, P_2O_5 and F, in phosphogypsum.

It can be suggested that Zn(II)-loaded phosphogypsum, after adsorption procedure, can be disposed by the stabilization process. As known, stabilization is a process employing additives (reagents such as cement, lime) to reduce the hazardous nature of waste by converting the waste and its hazardous constituents into a form to minimize the rate of contaminant migration into the environment, or to reduce the level of toxicity [38]. The precondition of phosphogypsum by lime milk may be useful for stabilization of Zn(II)-loaded phosphogypsum. For example, it may decrease stabilization cost by decreasing lime requirement. Moreover, it can be said that the stabilization process may not be required. Since the Zn(II) may be retained in the form of insoluble hydroxide salts within lime-preconditioned phosphogypsum, Zn(II)-loaded phosphogypsum after adsorption can be disposed, e.g. landfilling or utilised as building or road making materials, without the suspect on the leachability of Zn(II).

3.3. Adsorption isotherms

The equilibrium data for the adsorption are commonly known as adsorption isotherms. It is necessary to know them in order to compare the effectivities of different adsorbent materials under different operational conditions, and to design or optimise an adsorption system [39–41]. Several isotherm equations have been suggested to describe the modelling of the adsorption systems. However, the most commonly used models among them are Langmuir and Freundlich models for the single and binary cases [28].

In this study, Langmuir and Freundlich adsorption models were used to determine the adsorption capacity of phosphogypsum for Zn(II). The following equations were used for describing the Langmuir and Freundlich isotherms [20,42]:

Langmuir isotherm:

$$q = \frac{bq_m C_e}{1 + bC_e} \tag{2}$$

$$\frac{C_e}{q} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{3}$$

where C_e is the equilibrium metal concentration (mg L^{-1}), q the mass of the contaminant adsorbed per unit weight of the adsorbent (mg g^{-1}), q_m indicates the adsorption capacity of the adsorbent (mg g^{-1}) and b is the Langmuir isotherm constant (L mg^{-1}).

Freundlich isotherm:

$$q = KC_e^{1/n} \tag{4}$$

$$\log q = \log K + \frac{1}{n}\log C_e \tag{5}$$

where C_e is the equilibrium metal concentration (mg L^{-1}), q the mass of contaminant adsorbed per unit weight of the adsorbent (mg g^{-1}), and K (mg g^{-1}) and n are constants, indicating the adsorption capacity and adsorption intensity, respectively.

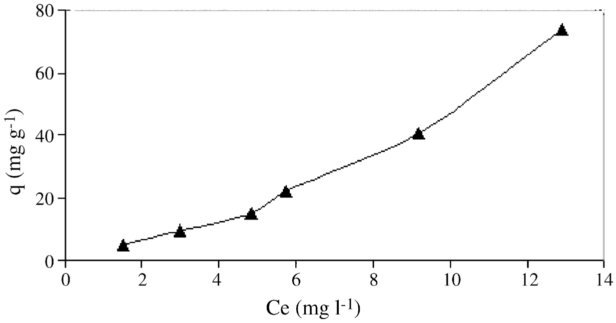

Fig. 5. Equilibrium curve for the adsorption of Zn(II) on phosphogypsum (Initial concentration of Zn(II), 50 mg L^{-1}; contact time, 45 min; pH 9.5).

Adsorption isotherm for Zn(II) adsorption from aqueous solution on the phosphogypsum is presented in Fig. 5.

The adsorption constants and correlation coefficients of the Freundlich and Langmuir isotherm were given in Table 2. As known, the applicability of the Langmuir isotherm suggests the monolayer coverage. The correlation coefficients of Freundlich and Langmuir models are 0.9893 and 0.9238, respectively. Therefore, the Freundlich isotherm is well fitted with the experimental data rather than the Langmuir isotherm and it cannot be mentioned about the monolayer coverage of Zn(II) ions on phosphgypsum.

When the n value of Freundlich (adsorption intensity) is high, the slope defined as $1/n$ decreases. Therefore, the affinity becomes low. In addition, highly low "n" values close to zero indicate the more heterogenous systems [43]. The experimental low adsorption intensity values (<1) suggests that the phosphgypsum possesses a heterogenous surface with identical adsorption energy in all sites [33,44,45] and the adsorbed Zn(II) ions interact only with the active site but not with other [46].

The Freundlich constant $1/n$ is also an indicator for the adsorption strength and a measure of the deviation from linearity of the adsorption. If $1/n$ is equal to unity, the adsorption is linear [47]. When $1/n > 1$ or becomes larger ($1/n \gg 1$), the adsorption bond becomes weak. As a result, it can be concluded that as the $1/n$ value for the adsorption by lime-pretreated phosphogypsum is more than unity, a physical adsorption rather than chemical is probably dominant in Zn(II) adsorption by lime-pretreated phosphogypsum [48].

3.4. The comparison of the adsorption capacities of phosphogypsum and various low-cost adsorbents

The Freundlich constants for the adsorption of Zn(II) by some natural materials, bioadsorbents, and activated carbons

Table 2
Freundlich and Langmuir parameters for the Zn(II) adsorption by phosphogypsum

Freundlich model			Langmuir model		
K (mg g^{-1})	n	r	q_m (mg g^{-1})	b (L mg^{-1})	r
2.5698	0.8000	0.9893	−77.5194	−0.0372	0.9238

r: Correlation coefficient.

Table 3
The Freundlich constants for Zn(II) adsorption by various adsorbents

Adsorbents	K (mg g^{-1})	1/*n*	References
Low-cost adsorbents			
Natural bentonite	2.28–8.44	0.20–0.48	[8]
Residues of banana peels	1.38	1.34	[16]
Residues of orange peels	1.43	1.33	[16]
Treated oil shale ash	0.20	2.54	[49]
Low-grade phosphate	1.69	0.45	[28]
Sea nodule residue	4.52–9.58	0.24–0.26	[50]
Crop milling waste (black gram husk)	0.96–0.99	0.45	[19]
Rice bran	1.34	2.38	[33]
Bioadsorbents			
Kudzu (*Pueraria lobata* ohwi)	0.97	0.61	[51]
Fungus *Mucor rouxii* (live biomass)	3.42	0.4	[25]
Fungus *Mucor rouxii* (pre-treated biomass)	1.94–2.07	0.61–0.89	[25]
Activated carbons			
Bagasse carbon	0.77–6.04	0.28–0.49	[7]
Phosphoric acid-activated pecan shell carbon (PSA)	13.9	0.04	[52]
Carbon dioxide-activated pecan shell carbon (PSC)	6.62	1.30	[52]
Steam-activated pecan shell carbon (PSS)	7.38	2.80	[52]
Commercial carbon, Filtrasorb-200 (from Calgon Carbon Co.)	0.29	0.80	[52]
Commercial granular activated carbon Fitrasorb-300 (from Calgon Carbon Co.)	1.83	0.30	[30]
Commercial granular activated carbon Fitrasorb-400 (from Calgon Carbon Co.)	1.02–2.88	0.35–0.49	[30]
Commercial C carbon (from Carbones Mexicanos)	10.05–10.59	0.15–0.18	[30]
Commercial carbon Centaur HSL	0.81	0.55	[30]
Phosphogypsum	2.57	1.25	This study

used before [7,8,16,19,25,28,30,33,49–52] and adsorbent used in the present study were given in Table 3.

Although direct comparison of phosphogypsum used with other reported adsorbents is difficult due to the varying experimental conditions employed in those studies, the data showed that phosphogypsum has generally a higher adsorptive capacity. However, the value of adsorption capacity was lower in phosphogypsum than in natural bentonite [8], sea nodule residue [50], live fungus *M. rouxii* biomass [25], PSA, PSC, PSS [52] and commercial C carbon [30].

For Zn(II), discharge standards into receiving water bodies defined for various industrial categories vary from 0.5 to 12 mg L^{-1} [53,54]. Thus, discharge requirements established for environmental legislation in Turkey can be matched using lime-preconditioned phosphogypsum. Also, it can be said that the discharge requirements to the other low-cost adsorbents (e.g. PAN-immobilized fungal biomass, sheep manure waste, fly ash, scoria) cited above can be matched.

4. Conclusions

In present study, it was observed that Zn(II) adsorption is highly dependent on pH. In addition, phosphogypsum dosage and initial Zn(II) concentration are effective on Zn(II) adsorption. Freundlich model gives a better fit.

It can be concluded that lime-preconditioned phoshogypsum can be used effectively for removal of Zn(II) from aqueous media and it can be considered as an alternative approach for treatment of aqueous solutions polluted by Zn(II). Indeed, this method can be considered as a simple way in respect of handling and economical point of view since lime-preconditioned phoshogypsum is a waste material from dihydrate wet phosphoric acid process in fertilizer plants. It is well known that phosphogypsum is generally stored in the vicinity of the plant until a suitable and economical method of disposal is devised. Thus, its use in Zn(II) removal can be also considered as a way of disposal.

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