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Adsorption of cadmium from aqueous solution by phosphogypsum

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Abstract

In the present study, the adsorption of cadmium on phosphogypsum, a waste material from the manufacture of phosphoric acid by wet process, was studied. Before batch adsorption study, phosphogypsum was pre-conditioned by milk of lime. Effect of initial pH on cadmium adsorption was investigated. It was found that cadmium adsorption was dependent on solution pH and maximum cadmium removal was observed in the pH range of 9.5 and 11.5. The Langmuir and Freundlich theories were used to describe the cadmium adsorption process, and the Freundlich isotherm showed the best fit to the process. Maximum adsorption capacity of lime-preconditioned phosphogypsum was found to be 131.58 mg/g.
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Keywords: Adsorption; Cadmium; Isotherm; Phosphogypsum; Wastewater

1. Introduction

Nowadays, various metals are discharged into the water bodies. The sources of trace metals are associated with human activities. Cadmium (Cd) like as the other heavy metals can be introduced into surface waters in amounts significant to human health by industrial effluents [1]. Cd, which is very toxic, can cause serious damage to the kidneys and bones. Itai-itai disease, renal damage, emphysema, hypertension and testicular atrophy are all harmful effects of cadmium [2]. The major sources of cadmium are industrial waters such as metal plating, cadmium-nickel batteries, phosphate fertiliser, mining, pigments, stabilisers and alloys [3].

The methods used to remove heavy metal ions are chemical precipitation, adsorption, ion-exchange, reverse osmosis, electrodialysis, electrochemical reduction, etc. Adsorption process is the most frequently applied method in industries. A lot of studies on this process have been carried out [4]. Although the use of activated carbon as an adsorbent on metal removal has been found to be successful, activated carbon is an expensive adsorbent especially for developing countries. The usage of agricultural residues or industrial by-product as alternative adsorbent for activated carbon has therefore received considerable attention. Many materials such as waste Fe(III)/Cr(III) hydroxide [5], red mud and fly ash [6], processed solid residue of oil mill products [7], spent grain [8], seafood processing waste sludge [9], treated *Pinus pinaster* bark [10], sawdust of *Pinus sylvestris* [11], montmorillonite, kaolin, tobermorite, magnetite, silika gel and alumina [12], brown, green and red seaweeds [13], tea-industry waste [14], calcite and hydroxyapatite [15] and waste materials as refuse concrete, waste paper and charcoal, and natural indigenous rocks as andesite, limestone, granite and nitrolite [16], olive cake [17], bagasse fly ash [18,19] and rice husk ash [19] have been tested for Cd(II) removal from water systems by various researchers.

In this work, an attempt has been made to adsorb Cd(II) from aqueous media by pre-conditioned phosphogypsum. Firstly, the physical and chemical characterization of the adsorbent was performed. In batch adsorption studies, the effect of pH on Cd(II) removal was investigated. Two commonly used equilibrium models, which are Langmuir and Freundlich, have been applied to the experimental data.

Phosphogypsum has been used for the removal of lead [20,21] and zinc [22] from aqueous solutions. In these studies, it was observed that it has good adsorptive properties for lead and zinc. Phosphogypsum is a by-product of the phosphate fertiliser industry, which is produced in large quantities worldwide by dehydrate wet phosphoric acid process. It has no apparent com-

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mercial value. Its accumulation at industrial sites does in fact pose a disposal problem.

2. Materials and methods

Phosphogypsum was obtained from TÜGSAŞ Fertiliser Plant in Samsun, Turkey. It was sieved through 45 and 65 mesh, respectively. The phosphogypsum fraction retained on the 65 mesh was collected and this fraction was used as the adsorbent in our study.

Phosphogypsum was subjected to pre-conditioning by milk of lime before using in the experimental studies. To neutralize the water insoluble impurities in phosphogypsum with milk of lime, as described by Ölmez and Yılmaz [23], it was firstly mixed with 0.4% milk of lime, a suspension of 14% was obtained and stirred for 5 min at 20 °C.

Some physical and chemical characteristics of the raw (unconditioned) phosphogypsum have been reported elsewhere [21,23]. In this study, physical characteristics such as surface area, pore size distribution, particle size distribution, porosity and density of the lime-preconditioned phosphogypsum are determined. These analyses were carried out in the METU Central Laboratory-Training Centre in Ankara, Turkey.

The structural characterization of phosphogypsum was performed by ATR technique on a Perkin-Elmer Spectrum One FT-IR spectrometer between 4000 and 650 cm^{-1} with 6 scans. The morphological characterization of adsorbent was carried out by a Jeol JSM-5600 scanning electron microscope (SEM).

An ATI-UNICAM 929 model Flame Atomic Absorption Spectrophotometer (FAAS) was used for the determination of Cd(II) ions. Cd(II) stock solution (0.1 mol/L) was prepared by dissolving the appropriate amount of its nitrate salt. The standard solution for atomic absorption spectrophotometer was prepared with the stock Cd(II) solution. The calibration graph was constructed with 10 standard solutions containing in 0.1–20 μg/L of Cd(II). The range of linearity was determined to be 0.2–3 μg/L. Limit of detection (0.04 μg/L) and limit of quantification (0.09 μg/L) were evaluated as the concentration corresponding to 3 times and 10 times the standard deviation of the blank signal, respectively. All other reagents used were of AR grade. Deionised water was produced by ELGA Maxima Ultra Pure Water Systems.

Adsorption studies were conducted by the batch technique. A series of 250 mL Erlenmeyer flasks were used. The Erlenmeyer flasks were filled with 100 mL of Cd(II) solution. A known amount of adsorbent dosage was then added to each Erlenmeyer flask and agitated intermittently by mechanical shaking at 200 rpm (Clifton NE5 28D Model Shaking Water Bath). After the agitation, the supernatant solution was centrifuged at 1000 rpm for 5 min and the uptake of Cd(II) ion was determined by FAAS. pH of aqueous solution was adjusted using $\mathrm{HNO_3}$ and NaOH solution when necessary.

All the experiments were performed in duplicate, and average values are reported ($N = 4$, $\bar{X} \pm ts/\sqrt{N}$). The maximum error determined with 95% confidence level was 5%.

Table 1
Physical properties of the lime-preconditioned phosphogypsum

Properties	Values
Density ($\mathrm{g/cm^3}$)	0.970
Surface area (multipoint BET) ($\mathrm{m^2/g}$)	6.228
Total interparticle porosity (%)	0.037
Total intraparticle porosity (%)	8.983
Total porosity (%)	9.020
Bulk density ($\mathrm{g/cm^3}$)	1.486
Pore diameter range (Å)	14.630–1631.450
Particle size range (μm)	4.000–100.000
Particle size (surface weighted mean) (μm)	5.882
Particle size (volume weighted mean) (μm)	26.730

3. Results and discussion

3.1. Physical and chemical characterization of the adsorbent

In this study, the physical and chemical characterization of the adsorbent was performed so that it could help in the interpretation of the results of the batch adsorption studies.

Data including some physical characteristics (surface area, pore size distribution, particle size distribution, porosity and density) on lime-preconditioned phosphogypsum are presented in Table 1. As seen in Table 1, the lime-preconditioned phosphogypsum had a surface area of 6.228 $\mathrm{m^2/g}$. This value is lower than those exhibited by granular-activated carbon (700–1300 $\mathrm{m^2/g}$) or powdered-activated carbon (800–1800 $\mathrm{m^2/g}$) as it is common in this kind of low-cost adsorbents [24].

The isotherms of adsorption/desorption on the lime-preconditioned phosphogypsum are shown in Fig. 1. The adsorption data indicates Type III isotherms. Type III isotherm is characterized principally by heats of adsorption which are less than the heat of liquefaction of adsorbate. As adsorption proceeds, additional adsorption is facilitated because the adsorbate interaction with an adsorbed layer is greater than the interaction with the adsorbent surface [25].

Pores can be classified according to their sizes. According to this classification, pores are known as micropores

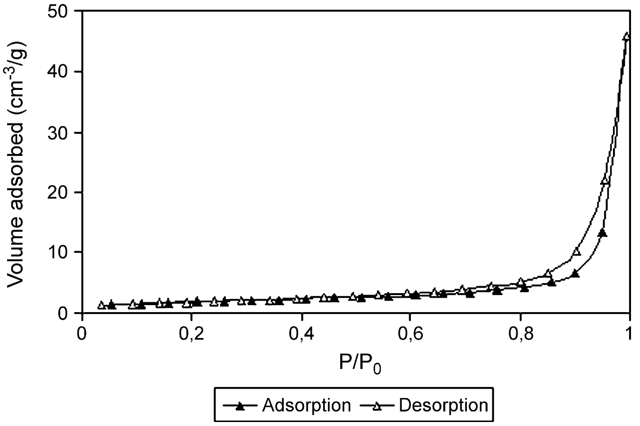

Fig. 1. Adsorption/desorption isotherm on the lime-preconditioned phosphogypsum.

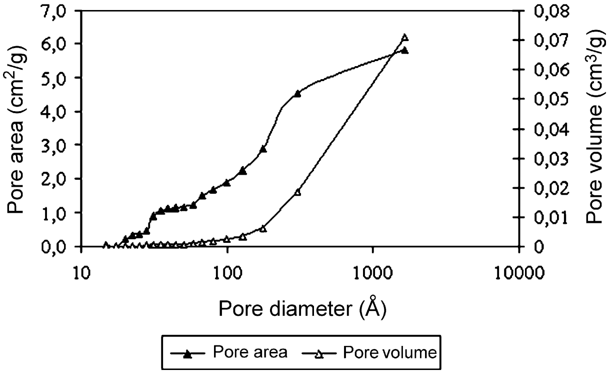

Fig. 2. Pore size distribution of the lime-preconditioned phosphogypsum.

(diameter < 20 Å) and mesopores (20 Å < diameter < 500 Å), and macropores (diameter > 500 Å) [26]. Due to the larger sizes of liquid molecules, the adsorbents for the adsorbates in liquid phase should have predominantly mesopores in the structure [27]. As can be seen in Fig. 2, although lime-preconditioned phosphogypsum exhibits a wide pore size distribution giving wide distribution of surface area, it consists of predominantly mesopores. The analysis of the BJH adsorption pore size distribution of lime-preconditioned phosphogypsum indicates that total pore area of the micropores, mesopores and macropores were about 1.47%, 78.32% and 20.21%, respectively.

As seen in Table 1, lime-preconditioned phosphogypsum had particle diameters between 4.000 and 100.000 μm. The average particle size of this adsorbent was 5.882 μm for surface weighted mean and 26.730 μm for volume-weighted mean.

Chemical characterization of the adsorbent surface was performed by FT-IR analysis. The spectra obtained for the raw and lime-preconditioned phosphogypsum are shown in Fig. 3 comparatively. The IR spectrum of phosphogypsum is well known [23], with the most intense peak around 1100 cm^{-1} (Fig. 3). The FT-IR spectra of raw and lime-preconditioned phosphogypsum are very similar to each other, but the peaks displayed slight shifts. Lime-preconditioned phosphogypsum has an additional weak band at 658 cm^{-1} which can be used to differentiate the two materials from each other.

The morphological characteristics of the adsorbent were evaluated by using a scanning electron microscope. SEM images from the raw and lime-preconditioned phosphogypsum are shown in Fig. 4. SEM observations of the raw and lime-preconditioned phosphogypsum reveal their surface textures. As shown in Fig. 4, there is a slight difference between the surface of the raw and lime-preconditioned phosphogypsum.

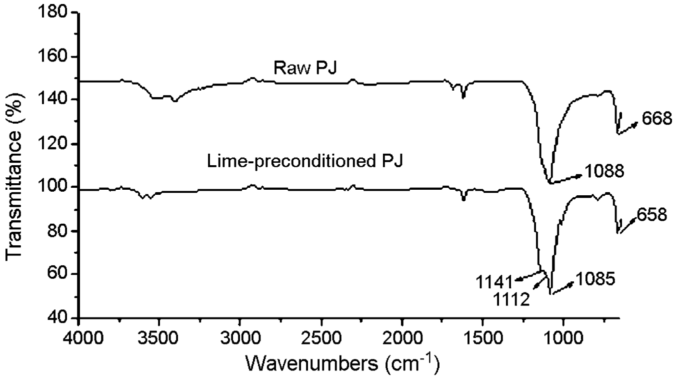

Fig. 3. FTIR spectra of the raw and lime-preconditioned phosphogypsum.

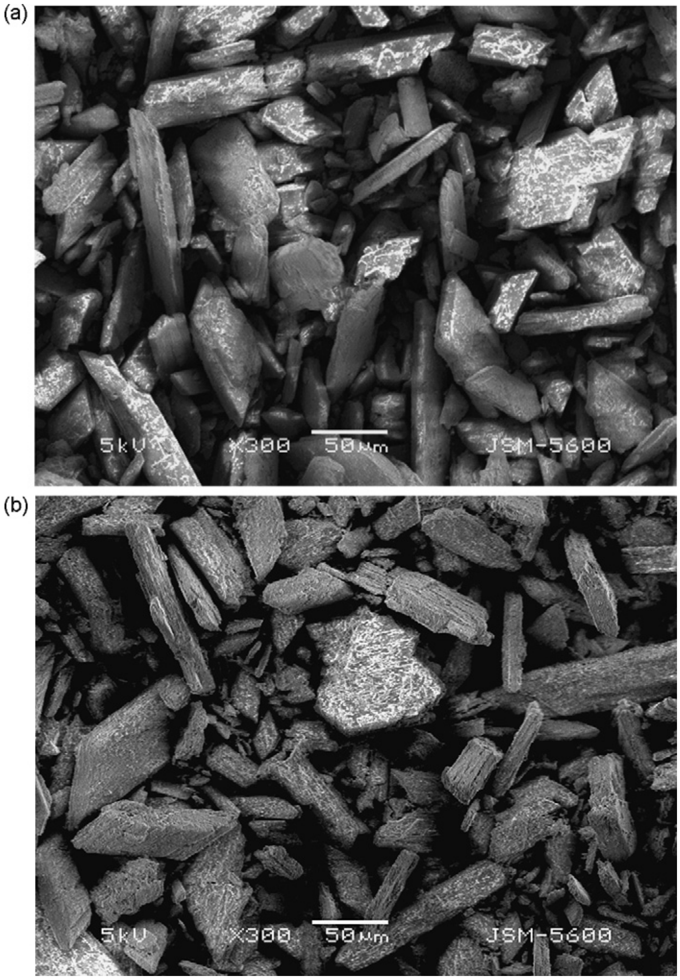

Fig. 4. Typical SEM micrograph of (a) the raw phosphogypsum and (b) the lime-preconditioned phosphogypsum.

3.2. *Effect of pH*

It is well known that metal ion removal by both non-specific and specific sorbents is dependent on pH between 2.8 and 10.0 [28]. Therefore in this study, in order to establish the effect of pH on the adsorption of Cd(II) ions onto the lime-preconditioned phosphogypsum, we repeated the batch equilibrium studies at different pH values in the range of 2.5–11.5. Fig. 5 illustrates the effect of pH on adsorption. It is evident that the adsorption of Cd(II) by the lime-preconditioned phosphogypsum begins at a pH value of around 8 with the gradual linear increase up to a value of 10.0. Similar behaviour with pH was reported by Singh et al. [29], and Evans et al. [30], Kadirvelu and Namasivayam [31], Srivastava et al. [18], Agraval and Sahu [32] for Cd(II).

The pH of the aqueous solution of Cd(II) affects its uptake on the lime-preconditioned phosphogypsum, and the uptake increases at higher pH values. This can be explained on the basis of proton-competitive sorption reactions. It can be said

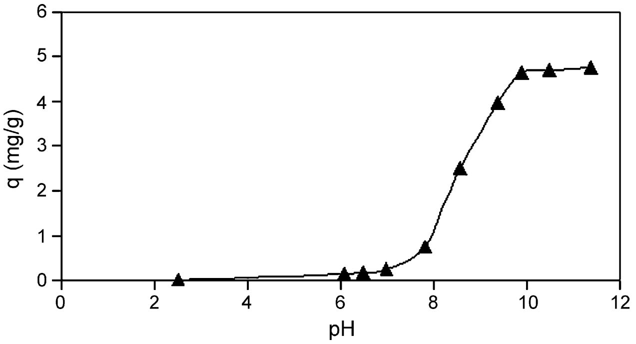

Fig. 5. Effect of initial pH on Cd(II) adsorption by the lime-preconditioned phosphogypsum (initial concentration of Cd(II): 50.0 mg/L; adsorbent dosage: 10.0 g/L: contact time: 2.0 h).

that at lower pH, H^+ ions compete with Cd(II) ions for the surface binding-sites of the adsorbent. Metal adsorption in acidic range has been described similarly by Namasivayam and Ranganathan [5], Doyurum and Çelik [17], Srivastava et al. [18], Singh et al. [29], Evans et al. [30], Kadirvelu and Namasivayam [31], Agraval and Sahu [32], Mohan and Singh [33], and Liu et al. [34]

When the pH was increased, the competing effect of H^+ ions decreased and the positively charged Cd^{2+} and $Cd(OH)^+$ ions hook up the free binding sites. Hence, the metal uptake was increased on the surface of the adsorbent with the increase in pH.

Cadmium species in deionised water are in the forms of Cd^{2+}, $Cd(OH)^+$, $Cd(OH)_2{}^0$, $Cd(OH)_{2(s)}$, etc. [35]. The concentration of the hydrolyzed cadmium species depends on the cadmium concentration, and the solution pH. Cd^{2+} ions are the only ionic species present in the solution for $pH < 6$ [18]. The dominant Cd(II) species at $pH > 8.0$ is $Cd(OH)_2$ and at $pH < 8.0$ is Cd^{2+} and $Cd(OH)^+$ [2,36].

It is known that precipitation plays a major role in removing of Cd(II) ions in alkaline range [18]. On the other hand, the precipitation of metal hydroxides into pores or spaces around the particles is hardly possible since the sorption process is kinetically faster than the precipitation [37,38]. Zn(II) adsorption by scoria in alkaline range has been described similarly by Kwon et al. [39]. Therefore, it can be said that Cd(II) removal by lime-preconditioned phosphogypsum was dominantly controlled by adsorption at pH values of about 9.0 but it could be slightly enhanced by cadmium hydroxide precipitation at $pH > 9.0$.

3.3. Adsorption isotherms

The general adsorption isotherm that can be used for describing the adsorption includes the Langmuir, Freundlich and Brunauer–Emmett–Teller (BET) type. The adsorption data were analysed using Freundlich [40] and Langmuir models [41].

Values of the Freundlich and Langmuir constants are given in Table 2. Correlation values (r) presented in Table 2 indicate that the adsorption data for Cd(II) removal fitted well with the Freundlich isotherm.

Table 2
Freundlich and Langmuir parameters for adsorption isotherms

Freundlich model			Langmuir model		
K (mg/g)	n	r	q_m (mg/g)	b (L/mg)	r
28.5102	1.4290	0.9962	131.5790	0.3333	0.9489

r: Correlation coefficient.

The value of the Freundlich constant showed a relatively easy uptake of Cd(II) ions with high adsorptive capacity of the lime-preconditioned phosphogypsum. In particular, “n” value, which is related to the distribution of bonded ions on the sorbent surface, is greater than unity, indicating that Cd(II) ions are, favourably, adsorbed under all the examined experimental conditions. The value of “n” between 1 and 10 also represents beneficial adsorption [42–44].

Based on the observed low adsorption intensity values ($1/n < 1$) it can be said that the lime-preconditioned phosphogypsum has heterogeneous surface with identical adsorption energy in all sites [45–47] and the adsorbed metal ion interacts only with the active site, but not with other sites [48].

The Freundlich constant $1/n$ is also a measure of the deviation from linearity of the adsorption. If $1/n$ is equal to unity, the adsorption is linear [49]. When $1/n < 1$, this expresses that the increased adsorption modifies the sorbent in a manner that increases the sorption capacity, such as forming new sites. If $1/n > 1$ or becomes larger ($1/n \gg 1$), the adsorption bond will be weak, and the value of q will be vary significantly with small changes in C_e. It can be said that as $1/n$ value of lime-preconditioned phosphogypsum is less than 1, chemical rather than physical adsorption seems to be dominant [50].

The values of the maximum adsorption capacities for the adsorption of Cd(II) on different adsorbents used in the literature with adsorbent of the present study are summarized in Table 3. Although direct comparison of the lime-preconditioned phosphogypsum with other adsorbent materials is difficult, owing to the differences in experimental conditions, it was found that the maximum adsorption capacity of lime-preconditioned phosphogypsum is higher than most adsorbents presented in Table 3.

Cd(II) ion adsorption isotherm of lime-preconditioned phosphogypsum is presented in Fig. 6.

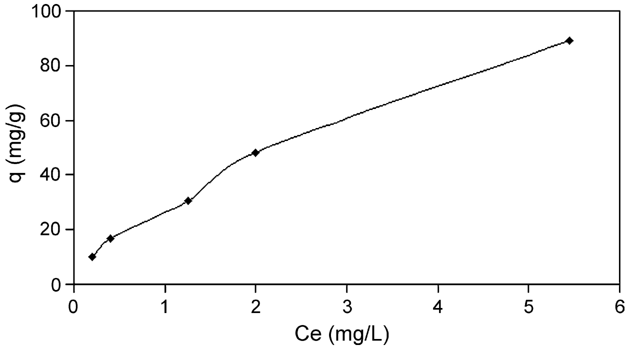

Fig. 6. Equilibrium curve for the adsorption of Cd(II) on the lime-preconditioned phosphogypsum.

Table 3
Adsorption capacities of various adsorbents

Adsorbents	q_m (mg/g)	References
Low-cost adsorbents		
Fe(III)/Cr(III) hydroxide-disposed as waste by industries	47.21	[51]
Tea-industry waste	11.29	[14]
Olive cake	10.56	[17]
Manganese nodule residue	416.00–476.00	[32]
Hazelnut shell	5.42	[52]
Carboxymethylcellulose	28.70	[53]
Bagasse fly ash	1.24–2.00	[54]
Low-grade phosphate	7.54	[55]
Black gram husk	39.99	[56]
Hematite	0.22–0.24	[29]
Kraft lignin	137.14	[57]
Wheat bran	0.63–0.70	[58]
Green coconut shell powder	285.70	[59]
Bioadsorbents		
Laminaria japonica (raw)	114.65–136.00	[60]
Laminaria japonica (pretreated)	131.52–151.75	[60]
Trametes versicolor (carboxymethylcellulose immobilized)	102.80	[53]
Trametes versicolor (heat inactivated)	134.50	[53]
Sargassum sp. biomass (dead)	98.00–120.00	[61]
Aspergillus niger (pretreated)	3.98–4.38	[62]
Aspergillus niger (live)	16.21–857.90	[62]
Mucor rouxii (pretreated)	8.36–20.31	[63]
Mucor rouxii (live)	8.46	[63]
Pantoea sp. TEM18	58.10	[64]
Ochrobactrum anthropi	37.30	[65]
Chinese herb *Pang Da Hai*	17.50	[34]
Sargassum baccularia (brown)	83.18	[13]
Sargassum siliquosum (brown)	82.05	[13]
Padina tetrastomatica (brown)	59.58	[13]
Chaetomorpha linum (green)	53.96	[13]
Gracilaria changii (red)	25.85	[13]
Gracilaria edulis (red)	26.98	[13]
Gracilaria salicornia (red)	17.99	[13]
Activated carbons		
Activated carbon derived from bagasse	27.47–49.07	[33]
Activated carbon derived from ceiba pentandre hulls	19.59	[43]
Activated carbon prepared from coconut coirpith	93.40	[31]
Activated carbon prepared from apricot stone	3.08–33.57	[66]
Activated carbon prepared from olive stone by $ZnCl_2$ activation	1.56–1.85	[67]
Activated carbon (Filtrasorb 400)	307.50	[62]
Carbon aerogel	400.80	[68]
Oak wood char	0.37	[69]
Pine bark char	0.34	[69]
Oak bark char	5.40	[69]
Carbon F-400	8.00	[69]
Calgon F-400	6.35	[70]
Lime-preconditioned phosphogypsum	131.58	Present work

3.4. Comparative study

Table 4
Comparison of the Cd(II) removal (%) from aqueous solution by lime, the raw phosphogypsum and the lime-preconditioned phosphogypsum (initial concentration of Cd(II): 50.0 mg/L; pH: 10.0; contact time: 120 min)

Material	Cd(II) removal (%)
Lime (0.28 g/L)	80.2
Raw phosphogypsum (10 g/L)	97.1
Lime-preconditioned phosphogypsum (10 g/L)	98.7

The Cd(II) removal by lime, raw phosphogypsum and preconditioned phosphogypsum was studied comparatively. The results of comparative study (Table 4) show that the percentage of Cd(II) adsorption by the raw phosphogypsum and preconditioned phosphogypsum is 97.1% and 98.7%, respectively. Cd(II) removal with lime (at equal quantity with that of lime used in pre-condition of phosphogypsum, 0.28 g/L) is 80.2%.

FT-IR spectra of the raw (at pH 10.0) and lime-preconditioned phosphogypsum (at pH 10.0 and 5.0) after Cd(II) adsorption are presented in Fig. 7 comparatively. It is shown that they are very similar but the peaks shifted slightly from each other.

SEM images from the raw (at pH 10.0) and lime-preconditioned phosphogypsum (at pH 10.0 and 5.0) after Cd(II) adsorption are shown in Fig. 8 comparatively. According to this micrograph, precipitation covering the particles of the lime-preconditioned phosphogypsum at pH 10.0 seems to occur. But, a similar trend is not observed for the particles of the raw phosphogypsum at the same pH. Also, as seen in Table 4, both forms of phosphogypsum at pH 10.0 are found to be equally effective in the removal of Cd(II) from aqueous solution. Therefore, it can be concluded that an additional mechanism for removal of Cd(II) may be precipitation as $Cd(OH)_2$. However, cadmium adsorption especially at low pH values plays an important role in the Cd(II) removal by lime-preconditioned phosphogypsum. It is estimated that phosphate groups on phosphogypsum may also be effective because the solubility of cadmium phosphate is much less than cadmium hydroxide for the adsorption of cadmium.

In comparison to the raw phosphogypsum, the lime-preconditioned phosphogypsum seems to be a more suitable adsorbent for the removal of Cd(II) from aqueous solution in practice because the pre-conditioning process neutralizes the water-soluble impurities (P_2O_5 and F) in the raw phosphogypsum. It is thought that neutralization of the water-soluble

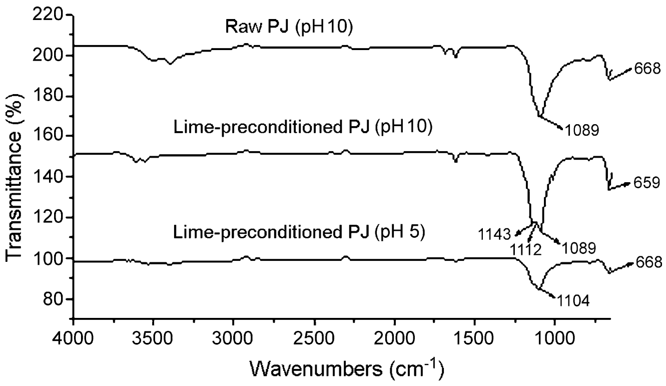

Fig. 7. FTIR spectroscopy of Cd(II) ion loaded adsorbent: (a) the raw phosphogypsum at pH 10.0, (b) the lime-preconditioned phosphogypsum at pH 10.0, (c) the lime-preconditioned phosphogypsum at pH 5.0.

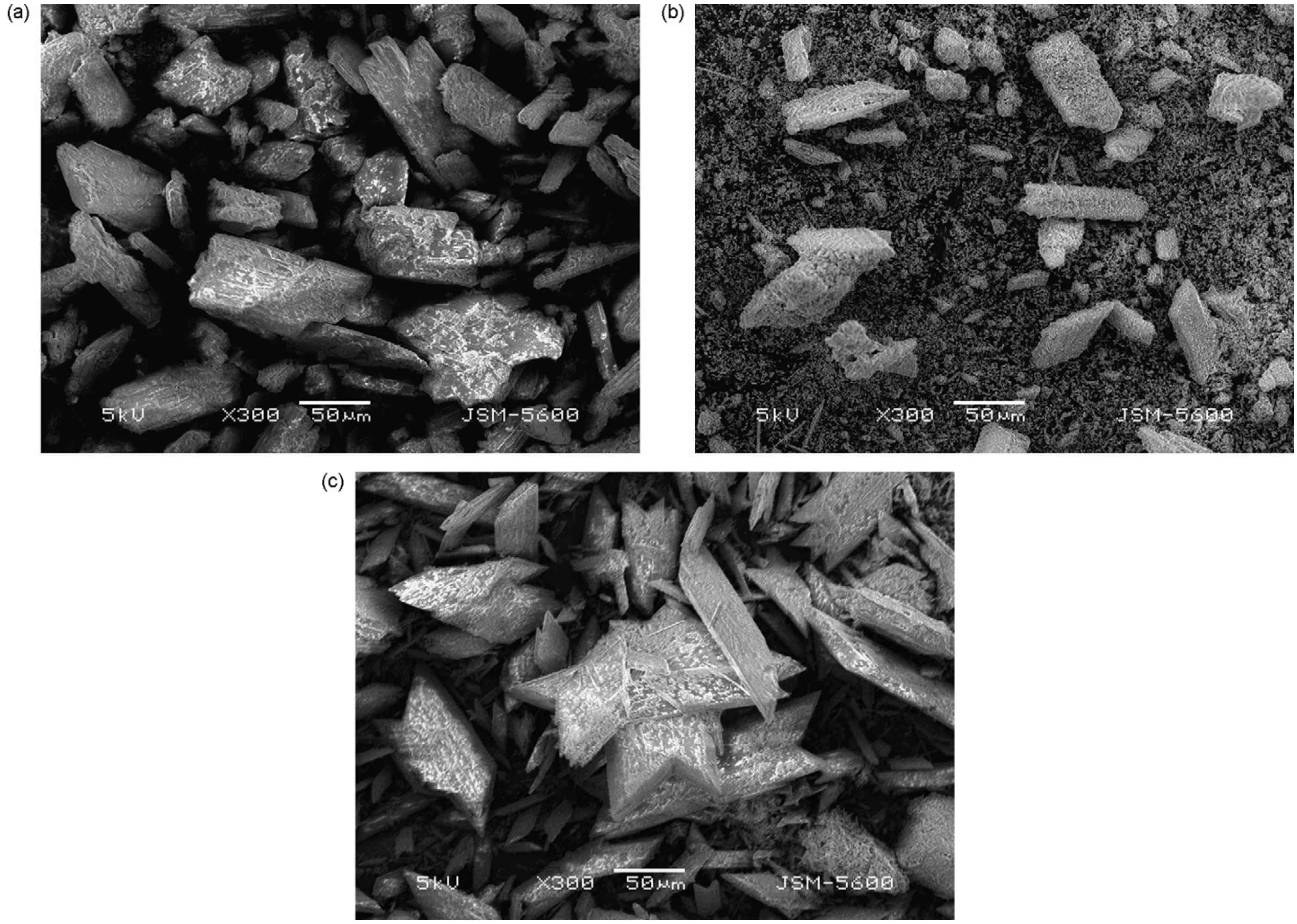

Fig. 8. Typical SEM micrograph after Cd(II) adsorption by: (a) the raw phosphogypsum at pH 10.0, (b) the lime-preconditioned phosphogypsum at pH 10.0, (c) the lime-preconditioned phosphogypsum at pH 5.0.

impurities in the raw phosphogypsum is important for disposal of Cd(II) loaded phosphogypsum after adsorption procedure. The phosphogypsum loaded with Cd(II) could be landfilled or utilised as building or road-making materials without the susceptibility of leachability of Cd(II).

3.5. Design of batch adsorption from isotherm data

The sorption process generally occurs by various mechanisms such as external mass transfer of solute onto sorbent followed by intraparticle diffusion. It is not possible to determine the rate-controlling step when there are not enough experimental data on the specific sorption application. Therefore, the most common method for predicting the adsorber size and performance is empirical design procedures based on sorption equilibrium conditions. Sorption equilibrium is a dynamic process when the rate of adsorption of the molecules is equal to their desorption rate. The physical chemistry involved may be complex and no single theory of sorption has been put forward to explain all the systems. Sorption isotherm relations were used to predict the design of single-stage batch-sorption systems using the data under equilibrium conditions [71–73].

Fig. 9 shows the plot between the predicted amount of lime-preconditioned phosphogypsum required to remove Cd(II) solutions of initial concentration 50 mg/L for 90%, 80%, 70%, and 60% Cd(II) removal at different solution volumes (1, 2, 3, 4, 5, 7, 10 L). For a single-stage batch-sorption system, the design procedure is outlined.

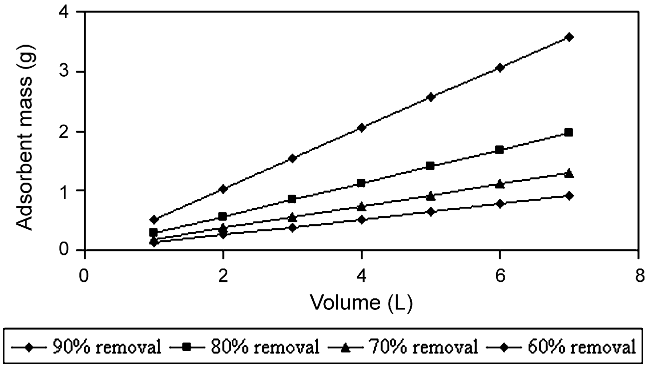

Fig. 9. Adsorbent mass (*M*) against volume of solution treated (L).

3.6. Cost estimation

The phosphogypsum, is a by-product discarded by a phosphate fertiliser industry. The cost of the adsorbent therefore arises only from the condition process of the adsorbent. The cost of adsorbent may be US\$ 1.5–2.0 t^{-1} depending on lime cost used in condition process. The known cost of activated carbon or ion-exchange resins is approximately US\$ 2000 and 4000 t^{-1} [74]. In Turkey, the cost of the cheapest commercial carbon is US\$ 1500 t^{-1}. Considering the above facts, the lime-preconditioned phosphogypsum can be considered as an economical alternative for the commercially available active carbon in removal of Cd(II) from industrial effluents.

4. Conclusion

The present study showed that lime-preconditioned phosphogypsum seems to be an efficient and economical adsorbent for the removal of Cd(II) ions from aqueous solution. pH was a critical parameter for the Cd(II) uptake. Maximum adsorption was found to occur in the pH range of 9.5 and 11.5. The adsorption isotherms fitted well by the Freundlich equation.

Experimental studies on Cd(II) adsorption by lime-preconditioned phosphogypsum are still being developed. Further data on Cd(II) adsorption from single (non-competitive) and binary (competitive) aqueous systems in continuous mode will be published in our future work. Investigation of Cd(II) adsorption from real wastewater are also planned.

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