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Multi-component sorption of Pb(II), Cu(II) and Zn(II) onto low-cost mineral adsorbent

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Abstract

Multi-component sorption studies were carried out for attenuation of divalent heavy metal cations (Pb^{2+}, Cu^{2+} and Zn^{2+}) by a low-cost mineral adsorbent from the aqueous solution. Kinetic and equilibrium batch-type sorption experiments were conducted under variable conditions for multi-component using low-grade (<12%P_2O_5) phosphate rock. Percentage of multiple heavy metal species removal increases with decreasing initial metals concentration and particle size. The equilibrium data were well described to a lesser extent by Freundlich model but Langmuir model seemed to be more appropriate with the fixation capacity obtained at room temperature for Pb^{2+}, Cu^{2+} and Zn^{2+} was 227.2, 769.2 and 666.6 $\mu mol\, g^{-1}$, respectively. Two simple kinetic models were tested to investigate the adsorption mechanism. Rate constants have been found nearly constant at all metal concentrations for first order. The comparison of adsorption capacity of low-grade phosphate rock decreases in multi-component system as compared to single component due to ionic interactions. X-ray powder diffraction (XRPD) technique was used to ascertain the formation of new metal phases followed by surface complexation. Used adsorbents have been converted into a value added product by utilizing innovative Zero-waste concept to solve the used adsorbents disposal problem and thus protecting the environment.
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Keywords: Multi-component sorption; Divalent heavy metal ions; Ionic interaction; X-ray powder diffraction; Zero-waste concept

1. Introduction

High concentration of heavy metals in surface water is generally associated with the disposal of industrial wastes. Metals containing industrial effluents constitute a major source of metallic pollution of the hydrosphere [1]. The metals are of special concern because they are non-degradable and therefore persistent. Lead is a more toxic element for human and animal lives. The presence of even low levels of lead in water is a concern primarily because it tends to bioaccumulate in the food chain. Numerous techniques and treatment technologies have been developed for the clean-up of waters contaminated with metals and trace metals. Among the available techniques, sorption has been used as one of the most practical methods. A sorbent must be eco-friendly, cost-effective, industrially viable and efficient for a wide range of concentration of different pollutant metals. Though activated carbon [2], silica gel [3] and activated alumina [4] are popular and effective adsorbents, their use is restricted for being not cost-effective. Mineral apatites (hydroxyapatite and fluorapatite) and different types of clays [5–7] have been utilized successfully for the removal of heavy metal ions such as lead, zinc and cadmium both collectively and separately in aqueous solutions using sorption techniques. Synthetic hydroxyapatite and high-grade (>30%P_2O_5) rock phosphates have been used in wastewater treatment and has a very high capacity for removing divalent heavy metal ions from water [8,9]. But hydroxyapatite and high-grade rock phosphates are not reported commercially viable because of their high costs. Therefore, recent studies have focused on the search of an inexpensive and efficient adsorbent.

For quite some time we are involved in utilizing inexpensive minerals such as low-grade phosphate rock, pyrophyllite, etc. very effectively as adsorbents for divalent heavy metal ions present as single species in aqueous solution [10,11]. Continuing

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our activities in this direction, we have taken up the studies on multi-component adsorption where heavy metals are collectively (Pb + Cu + Zn) present in the aqueous system using low-grade phosphate rock of Jhabua, Madhya Pradesh, India as adsorbent which is considered as waste for fertilizer industries because of its very low phosphate values. Jhabua phosphorite deposits of sedimentary origin were located by Geological Survey of India in 1973. There is a large unexploited deposit of low-grade phosphate rock at Jhabua.

The overall objectives of the present study were (i) to investigate the effects of adsorbent particle size, initial sorbate concentration and temperature; (ii) to evaluate the observed sorption capacity of rock phosphate, based on theoretical approach using adsorption isotherms; (iii) to ascertain the effect of ionic interaction; (iv) to elucidate the sorption mechanism; (v) to utilize Zero-waste concept for conversion of used adsorbents into value added products.

2. Material and methods

2.1. Sorbent

Representative samples of low-grade rock phosphate (francolite) from Jhabua (Madhya Pradesh) were collected for the present study with the help of M.P. State Mining Corporation, Bhopal, India. The samples (1.0 kg) were ground by Denver ball mill and sized by wet sieve analysis separately for experimental work. The representative ground sample after coning and quartering was subjected to wet chemical analysis. Based on sorption characteristics, the mineral sample of −105 + 75 μm size range was used for adsorption studies. The mineral sample of −105 + 75 μm size range was stored in desiccators until commencement of sorption experiments.

The physical properties such as porosity, hardness, specific gravity, surface area, porosity, CEC (Cation Exchange Capacity) and chemical composition of the adsorbent are shown in Table 1. The CEC value comes about 3.74 meq g^{-1} by addition of all the four exchangeable monovalent (Na: 0.770 and K: 0.159 meq g^{-1}) and divalent (Ca: 2.594, Mg: 0.215 meq g^{-1}) cations. The high CEC value results from the presence of higher amount of divalent EC (Exchangeable Cation, mainly calcium) in mineral adsorbent sample. X-ray diffraction analysis of francolite mineral sample reported the presence of mainly calcite, fluorapatite and quartz as described elsewhere [12,13]. Dolomite and iron oxide are the other associated gangue minerals present in minor amounts. The bulk chemical composition of mineral sample was analyzed by wet chemical method (Table 1). The surface area and adsorption average pore width of the selected fraction of rock phosphate sample were 7.285 m^2 g^{-1} and 95.7779 Å, respectively.

Table 1
Physical properties and chemical composition of the mineral adsorbent

Physical properties		Chemical composition	
Porosity (%)	49	P_2O_5	12.50
Surface area (m^2/g)	7.285	SiO_2	26.50
Specific gravity	2.7	CaO	32.60
Hardness	4.5	Fe_2O_3	1.59
Cation Exchange Capacity (meq g^{-1})	3.74	Al_2O_3	6.08
		MgO	0.06
		TiO_2	0.49
		F	1.06
		L.O.I.[a]	19.12

[a] Loss on ignition.

2.2. Analytical techniques

X-ray analysis of finely ground sorbent (rock phosphate) sample was done with the help of a Philips X-ray machine (Model PW 1710). The surface area and adsorption average pore width of the selected fraction of rock phosphate sample were determined by the N_2 gas BET analysis using a Micromeritics Chemisorption ASAP 2020. Electric rotary shaking machine and Systronic digital pH meter were used for equilibration and pH measurement of the solutions. Heavy metals analysis were carried out by using a GBC-902 Atomic Absorption Spectrophotometer (AAS).

2.3. Sorption experiments

All reagents used were of analytical (Merck) grade. Test solutions of heavy metal ions for both cases of single and multiple species adsorption were prepared from their nitrate salts by serial dilution of stock lead, copper and zinc ion solution (1000 mg l^{-1} each) using deionized distilled water (Milli-Q, Milipore). Blank solution of deionized distilled water was analyzed by AAS to ensure that it did not contain lead, copper and zinc ions.

For preparing multiple species (Pb + Cu + Zn) stock solution, the amounts of nitrate salts of all the three metal ions required for a particular concentration were calculated and the appropriate amounts of each salts were taken to a standard flask (1 l) in the molar ratio of 1:1:1 and made up the solution up to the mark. The concentration (mg l^{-1}) referred in the multi-metal case, is the mixed concentration referred to individual concentration of the same value. After adsorption experiments, filtered solution was acidified with HNO_3 for AAS analysis of cations. Kinetic and equilibrium batch-type sorption experiments were conducted under variable conditions for multi-component. For all batch types of sorption experiments, blank experiments were carried out with the same experimental procedure to check the extent of adsorption by the glass flasks. The kinetic and equilibrium experiments were performed in different batches. 0.5 g adsorbent mineral samples were equilibrated separately with 100 ml solutions of different concentrations (10, 50, 100 and 500 mg l^{-1}) of multi-component ($Pb^{2+} + Cu^{2+} + Zn^{2+}$). The suspensions were shaken on a mechanical shaker fitted with thermostat at room temperature (30 °C) for 10 min followed by 30 min quiescent contact time. Suspensions were then filtered through Whatmann filter paper (No. 42). The filtrates were analyzed for Pb^{2+}, Cu^{2+} and Zn^{2+} final concentration. For arriving at the required quiescent time needed for attainment of adsorption equilibrium, the quiescent time was varied between 10 and 40 min at intervals of 5 min for different initial lead, copper and zinc ion concentration. The equilibrium was observed to reach

within 30 min time. Three random tests were done for different concentrations to check the reproducibility of the results. For each set of experiments the pH of solution just before adding the adsorbent and after shaking with adsorbent were recorded. No imposition of any ionic strength was imposed during course of experiments, i.e. all the experiments were carried out under natural conditions.

2.4. Kinetic studies in multi-metal scenario

In order to determine kinetic sorption parameters, the obtained kinetic sorption data were fitted to the Lagergren rate equation which is one of the most widely used sorption rate equations [14].

$$\log(q_e - q_t) = \frac{\log q_e \cdot k_{ad} \cdot t}{2.303} \quad (1)$$

where k_{ad} (min^{-1}) is the rate constant of pseudo-first-order adsorption, q_e ($\mu mol\, g^{-1}$) is the amount of metal ion sorbed at equilibrium and q_t ($\mu mol\, g^{-1}$) is the amount of metal ion sorbed at any time t (min) on the adsorbent surface.

The experimental data were also fitted for pseudo-second-order adsorption. The second-order rate expression and can be expressed as [15]:

$$\frac{t}{q_t} = \frac{1}{k_1 q_e^2} + \frac{t}{q_e} \quad (2)$$

Equilibrium relationships between adsorbent and adsorbate are described by sorption isotherms usually as the ratio between the quantity sorbed and that remaining in the solution at a fixed temperature. Experimental sorption isotherm data are often described and modeled by the relations developed by Langmuir and Freundlich. The data obtained were fitted to Langmuir and Freundlich adsorption isotherms, respectively.

The Langmuir equation is expressed in a linear function as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 \cdot b} + \frac{C_e}{Q_0} \quad (3)$$

where q_e ($\mu mol\, l^{-1}$) is the amount of metal ions adsorbed at equilibrium, C_e ($\mu mol\, l^{-1}$) is the equilibrium concentration of metal ions, Q_0 and b are Langmuir constants related to monolayer sorption capacity and sorption energy, respectively.

The Freundlich model is described by the following linear equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

Both K_F and n are empirical constants being indicative of the extent of adsorption (sorption capacity) and the degree of non-linearity between solution and concentration.

3. Results and discussion

3.1. Effect of adsorbent particle size

Particle sizes ranging from as coarse as −420 μm to as fine as −53 μm were considered for the present set of experiments under the conditions of 0.5 g of mineral adsorbent, 100 ml of 100 mg l^{-1} lead solution and 30 min as conditioning time. It is observed that percent attenuation increases (25.5–93.0) with decrease in fineness or particle size (−420 + 210 to −105 + 75 μm). Percent attenuation is independent of fineness below particle size of −105 + 75 μm which is in accordance with the author's earlier work [13].

3.2. Effect of initial sorbate concentration

In order to investigate the effects of initial heavy metal ions concentration on their removal, four different sorbate mixed concentrations (5, 10, 50 and 100 mg l^{-1}) were prepared and tested with phosphate rock adsorbent (−105 + 75 μm in size) for sorption studies. Fresh stock of multi-metal solution was prepared for each set of multi-metal sorption experiments (four concentrations). The results are shown in tabular form (Table 2a). The removal percentage of each heavy metal ions decreased with increasing concentration. This behavior is well known as 'loading effect' which describes the extent to which the total number of sorption sites is occupied by the sorbate. However, the removal capacity of sorbent (or the uptake of each metal ions by adsorbent) increased with initial metal ions concentration. It is in agreement with findings of Prasad et al. and Jang-Soon et al. [10,16].

Distribution coefficients (K_d) were calculated for each metal ion to assess the effect of initial ion concentration for the case of multi-metal and single-metal ion as depicted in Tables 2b and 2c. For each metal ion (Pb, Cu and Zn), the values of coefficients decreases gradually with increase in concentration. This behav-

Table 2a
Effect of initial ions concentration on attenuation of heavy metal ions present as multiple species ($Pb^{2+} + Cu^{2+} + Zn^{2+}$)

Initial ions concentration (Pb + Cu + Zn) (mg l^{-1})	Final ions concentration (mg l^{-1})			% Attenuation			Removal capacity (mg metal/g adsorbent)			pH		
	Pb	Cu	Zn	Pb	Cu	Zn	Pb	Cu	Zn	pH_1	pH_2	pH_3
5.0	0.007	0.06	1.94	99.8	98.8	61.2	0.998	0.988	0.612	5.87	6.66	7.11
10.0	0.03	4.7	4.3	99.7	53.0	57.0	1.998	1.06	1.14	5.23	6.48	6.97
50.0	11.0	20.0	30.5	78.0	61.0	39.0	7.80	6.0	3.9	4.31	5.74	6.02
100.0	53.0	51.5	75.0	47.0	48.5	25.0	9.40	9.7	5.0	2.39	3.26	3.98

Conditions: 0.5 g (−105 + 75 μm) of phosphate rock, 100 ml of initial solution volume, 30 min as conditioning time. pH_1 refers to initial pH of test solution without sorption. pH_2 refers to pH of test solution after shaking for 10 min. pH_3 refers to pH of filtrate solution after sorption experiment.

Table 2b
Distribution coefficient for multi-metal solution

Initial ions concentration (Pb + Cu + Zn) (mg l^{-1})	Distribution coefficient, K_d		
	Pb	Cu	Zn
5.0	713.2	82.3	1.57
10.0	332.3	1.12	1.32
50.0	3.54	1.5	0.63
100.0	0.866	0.961	0.33

ior of sorbent may be attributed to 'loading effect' as discussed above. However, the value of distribution coefficient, K_d, has larger values for the case of single-metal in comparison to multi-metal. This may be attributed to higher removal capacity of rock phosphate for the case of single-metal ion case with respect to multi-metal ion case.

3.3. Solution pH behavior

The present study was carried out in natural conditions, i.e. no effort was made to control the solution pH during the experiments and also no ionic strength was imposed. The initial pH (pH_1) of metal solutions, pH of test solution after shaking for 10 min (pH_2) and final pH (pH_3) of filtrate at sorption equilibrium were measured for each metal concentration. As shown in Tables 2a–2c, the pH values of all the test solutions decreased with increase in metal concentration, but in the identical metal concentration, they increased gradually after equilibration with sorbent. The decrease of pH at higher metal concentration may be due to metal–ion complexation which produces more H^+ ions and this can cause more phosphate rock dissolution followed by adsorption through ion-exchange.

3.4. Modeling of the kinetics (half life and order of reaction)

Perusal of the literature has revealed majority of the adsorption kinetic studies by mineral adsorbents to be governed by pseudo-first-order rate and diffusion controlled mechanism [17]. For the present investigation, the sorption kinetic rates and metal recoveries were estimated by both pseudo-first- and second-order models. To check the validity of these two models, the kinetics were studied for different initial metal concentrations (48.2, 241.0 and 482.0 μmol l^{-1} for lead, 157.3, 786.2 and 1573.0 μmol l^{-1} for copper and 152.9, 764.5 and 1527 μmol l^{-1} for zinc) as shown in Table 3. All the above different concentrations of individual metals expressed in μmol l^{-1} refers to 10, 50 and 100 mg l^{-1} of each metal concentration.

Table 2c
Distribution coefficient for single-metal solution

Initial ions concentration (mg l^{-1})	Distribution coefficient, K_d		
	Pb	Cu	Zn
5.0	1665.6	124.0	37.46
10.0	1249.0	99.0	32.3
50.0	415.6	9.0	4.0
100.0	13.28	5.25	3.2

The 'half-life time' was chosen as the basis for the most suitable model for the present case because it is well known that for first-order reaction kinetics, half-life time remains constant whatever the initial sorbate concentration is under consideration. Each kinetic parameter was evaluated for first- and second-order reactions as shown in Table 3. Half-life time was found to be nearly constant with the increasing metal concentration (8.35, 9.24 and 9.74 for Pb^{2+}, 8.3, 8.67 and 9.5 for Cu^{2+} and 7.05, 7.88 and 8.31 for Zn^{2+}) thus validating the assumption of first-order sorption mechanism rather than a second-order one. Half-life was checked also for second order. A lot of variation (from 0.319 to 1.4 for Pb^{2+}, from 0.25 to 1.21 for Cu^{2+} and 1.41 to 29.7 for Zn^{2+}) was observed for increasing concentration of metal ions.

The straight line fits of the pseudo-first-order [$\log(q_e - q_t)$ versus t, Eq. (1)] and pseudo-second-order [t/q_t versus t, Eq. (2)] model are shown in Figs. 1 and 2, respectively. The regression coefficients for these plots are very good. The rate constants, k_{ad}, for pseudo-first-order rate equations are found nearly constant for all the divalent metal ions under consideration.

3.5. Metal adsorption isotherms

Equilibrium sorption studies were performed to get the maximum metal adsorption capacities of the adsorbent in the concentration range from 144.6 to 482.0 μmol l^{-1} for lead, 471.9 to 1573.0 μmol l^{-1} for copper and 458.7 to 1529.0 μmol l^{-1} for zinc solutions at 303, 313, 323 and 333 °K. The adsorption data were analyzed by a regression analysis to fit the Freundlich and Langmuir isotherm models. Both these isotherms plots (Figs. 3 and 4) represented and were in good agreement with the experimental data and suggested that the metal ions sorbed form a monolayer coverage on the adsorbent surface. The coefficients of these two models were computed using linear least square fittings as shown in Table 4. The Langmuir parameters 'Q_0' and 'b' and the Freundlich parameters 'K_F' and '$1/n$' were computed with the respective determination of correlation coefficients, R^2. The constant, K_F, has comparatively higher values for lead than copper and zinc at all the temperatures studied in the present investigation. The values of monolayer sorption capacity, Q_0, increases with temperature for lead, copper and zinc.

On comparison it appeared that the equilibrium data were also well described to a lesser extent by Freundlich model but Langmuir model seemed to be more appropriate. As expected with the kinetic studies, the maximum fixation capacity, 'Q_0', was obtained at 333 °K for Pb^{2+} to be 416.6 μmol g^{-1}, for Cu^{2+} to be 1666.6 μmol g^{-1} and for Zn^{2+} to be 2000.0 μmol g^{-1}.

A comparison of Langmuir and Freundlich constants for single (in the absence of other metal ions) and multi-component adsorption (in the presence of other metal ions) of Pb(II), Cu(II) and Zn(II) has been shown in Table 5. Both Freundlich and Langmuir constants (K_F and Q_0) representing sorption capacity for the case of single component have higher values than multi-

Table 3
Kinetic parameters for metal adsorption onto the mineral adsorbent

Metal	First order			Second order			
	C_0 (μmol l^{-1})	k_{ad} (min^{-1})	R^2	v_o (μmol g^{-1} min^{-1})	k_1 (g min^{-1} μmol^{-1})	q_e (μmol g^{-1})	R^2
Pb^{2+}	48.2	0.0711	0.995	6.37	6.5×10^{-2}	9.897	0.997
Pb^{2+}	241.0	0.0829	0.970	6.05	2.95×10^{-3}	45.21	0.980
Pb^{2+}	482.0	0.0750	0.979	7.47	2.226×10^{-3}	57.93	0.977
Cu^{2+}	157.3	0.0799	0.952	0.808	5.4×10^{-4}	38.69	0.946
Cu^{2+}	786.25	0.0725	0.970	7.89	5.075×10^{-4}	124.73	0.941
Cu^{2+}	1573.0	0.0833	0.963	19.38	5.24×10^{-3}	192.2	0.969
Zn^{2+}	152.9	0.0928	0.998	0.751	2.20×10^{-4}	58.35	0.935
Zn^{2+}	764.5	0.0879	0.912	5.344	9.24×10^{-4}	76.03	0.928
Zn^{2+}	1529.0	0.0833	0.940	5.105	2.84×10^{-4}	134.0	0.916

Table 4
Langmuir and Freundlich parameters for metal adsorption onto the mineral adsorbent

Temperature (°K)	Pb^{2+}			Cu^{2+}			Zn^{2+}		
	Q_0 (μmol g^{-1})	$b \times 10^5$ (l mol^{-1})	R^2	Q_0 (μmol g^{-1})	$b \times 10^5$ (l mol^{-1})	R^2	Q_o (μmol g^{-1})	$b \times 10^5$ (l mol^{-1})	R^2
Langmuir									
303	227.2	9.66	0.981	769.2	7.29	0.998	666.6	5.6	0.989
313	285.7	2.75	0.974	909.1	1.95	0.991	1111	1.09	0.825
323	384.6	1.159	0.992	1111.1	0.958	0.986	1111	0.66	0.923
333	416.6	0.79	0.995	1666.6	0.402	0.880	2000	0.20	0.974

Temperature (°K)	Pb^{2+}			Cu^{2+}			Zn^{2+}		
	$1/n$	K_F (l g^{-1})	R^2	$1/n$	K_F (l g^{-1})	R^2	$1/n$	K_F (l g^{-1})	R^2
Freundlich									
303	0.237	54.07	0.996	0.438	33.18	0.995	0.370	40.85	0.992
313	0.413	15.13	0.931	0.67	5.82	0.980	0.726	3.06	0.952
323	0.542	6.72	0.941	0.679	3.93	0.980	0.888	1.33	0.962
333	0.562	5.03	0.913	0.881	1.32	0.963	0.986	3.77	0.986

component adsorption. Single component adsorption data refers to the work as described elsewhere [18].

3.6. Effect of ionic interaction

Adsorption in multi-component systems is much complicated because of the solute–surface interactions and competition of metal ions with each other. The results in Table 5 clearly show the presence of other metal ions by decreasing the constant (K_F and Q_0) values which reflects the interference of competing ions. The effect of ionic interaction [19] on the sorption process may be represented by the ratio of the sorption capacity of one metal ion in the presence of the other metal ions, Q^{mix}, to the sorption capacity of same metal ion when it is present alone in the solution, Q°, such that for:

$$\frac{Q^{mix}}{Q^\circ} > 1$$

the sorption is promoted by the presence of other metal ions,

$$\frac{Q^{mix}}{Q^\circ} = 1$$

Table 5
Comparison of Freundlich and Langmuir isotherm constants for single and multi-component adsorption of Pb^{2+}, Cu^{2+} and Zn^{2+} on phosphate rock at room temperature (30 °C)

Metal ions	Systems	Freundlich constants				Langmuir constants			
		K_F	$1/n$	R^2	K_F^{mix}/K_F	Q_0	$b \times 10^5$	R^2	Q^{mix}/Q°
Pb	Pb alone	58.26	0.461	0.971		282.90	98.36	1.00	
Cu	Cu alone	43.47	0.445	0.991		790.27	76.83	0.937	
Zn	Zn alone	42.64	0.427	0.981		716.0	55.25	0.962	
Pb	Pb + Cu + Zn	54.07	0.28	0.792	0.928	227.2	90.66	0.981	0.803
Cu	Pb + Cu + Zn	33.18	0.438	0.995	0.763	769.2	70.29	0.998	0.973
Zn	Pb + Cu + Zn	37.15	0.37	0.992	0.871	666.6	50.6	0.989	0.931

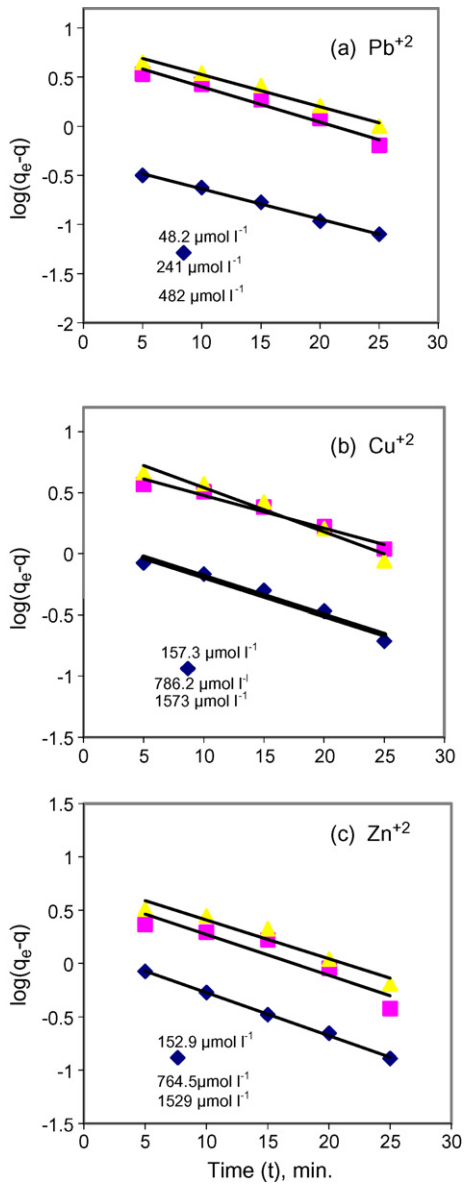

Fig. 1. Lagergren first-order kinetic plot for sorption of mixed divalent heavy metal species.

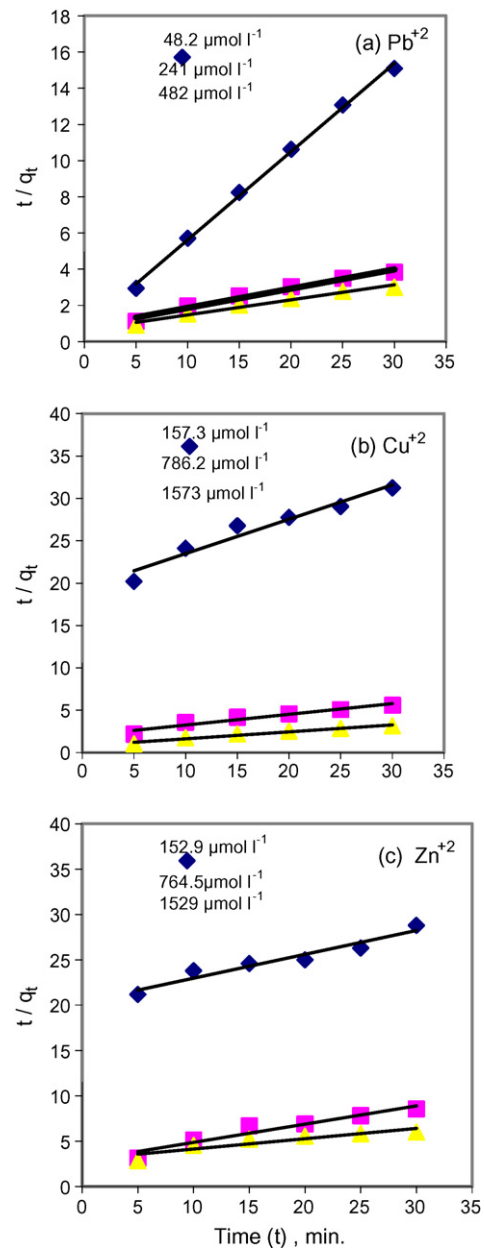

Fig. 2. Lagergren second-order kinetic plots for sorption of mixed divalent heavy metal species.

there appears no observable net interaction,

$$\frac{Q^{\text{mix}}}{Q^{\circ}} < 1$$

the sorption is suppressed by the presence of other metal ions.

The values of Q^{mix}/Q° are found to be <1 as shown in Table 5. These results are consistent with the sorption isotherms obtained for Pb(II), Cu(II) and Zn(II) in the absence and presence of various metal ions. Q^{mix} increased in the order (Zn(II) < Cu(II) < Pb(II)) for the adsorption of Pb(II), Cu(II) and Zn(II) in multi-component system. Overall, it may be concluded that the adsorption capacity of low-grade phosphate rock decreases in multi-component system as compared to single component. A comparison of removal capacities of phosphate rock in single as well as in multi-component sorption has been shown in Fig. 5. Single component sorption studies refer to author's previous work [13].

3.7. Sorption mechanism

Sorption is the loss of a chemical species from an aqueous solution to a continuous solid phase. Two of the principle mechanisms of sorption include adsorption, the two-dimensional accumulation of matter at the mineral–water interface; and precipitation, the three-dimensional growth of a solid phase [20].

Processes such as adsorbent dissolution, cation-exchange, metal complexation on adsorbent (phosphate rock) surface, followed by a new metal phase precipitation have been proposed

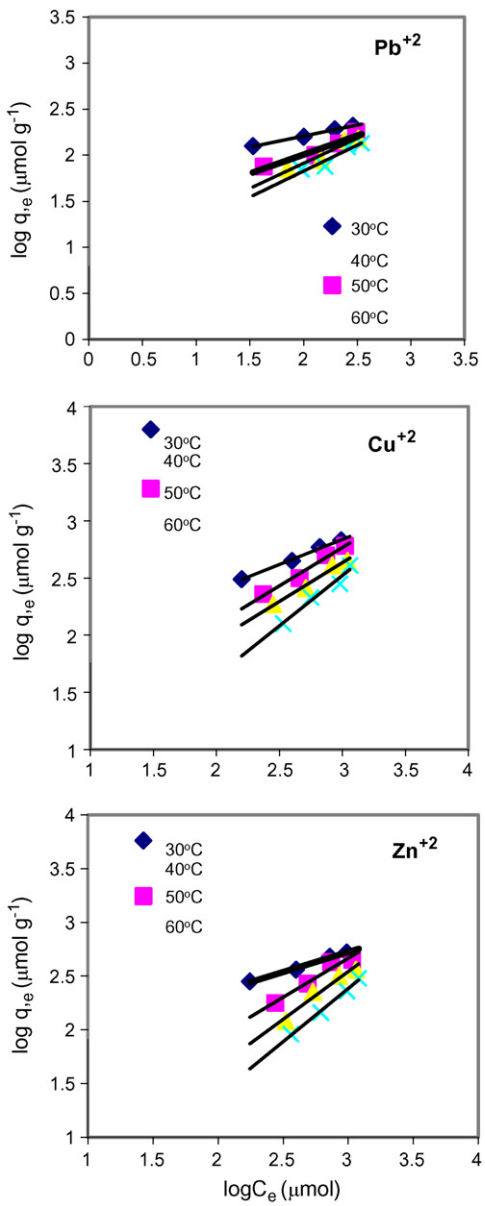

Fig. 3. Freundlich sorption isotherms for mixed divalent heavy metals at different temperatures (absorbent mass = 10 g l^{-1}, V = 100 ml, equilibration time, t = 30 min).

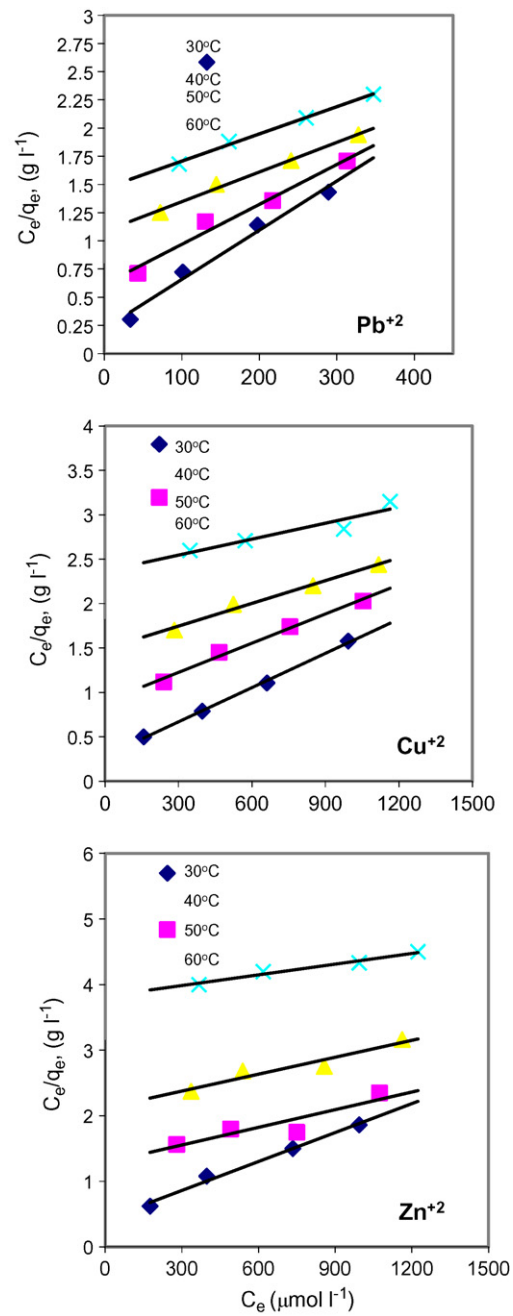

Fig. 4. Langmuir sorption isotherms for mixed divalent heavy metals at different temperatures (absorbent mass = 10 g l^{-1}, V = 100 ml, equilibration time, t = 30 min).

in order to describe the uptake of different metals from aqueous solution by synthetic hydroxyapatite (HA) and rock phosphate [21–23,8].

All the three metal ions (lead, copper and zinc) form amphoteric hydroxide because of their dual nature of acid–base reactions [24] as explained below:

$$Pb(H_2O)_2(OH)_2 + 2H_3O^+ = Pb(H_2O)_4{}^{2+} + 2H_2O$$

$$Zn(H_2O)_2(OH)_2 + 2H_3O^+ = Zn(H_2O)_4{}^{2+} + 2H_2O$$

$$Cu(H_2O)_2(OH)_2 + 2H_3O^+ = Cu(H_2O)_4{}^{2+} + 2H_2O$$

In the present study of sorption of heavy metal ions, initially the pH of the solution is governed by the concentration of lead/copper/zinc nitrate solution leading possibly to the formation of $Pb(H_2O)_2(NO_3)_2/Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O/Cu_5(OH)_8(NO_3)_2{\cdot}2H_2O$ which slowly get converted into $Pb(H_2O)_4{}^{2+}/Zn_5(OH)_8/Cu_5(OH)_8$ species. Further, as the pH changes from acidic to alkaline side, as explained in Tables 2a–2c, involving exchange as well as release of calcium ions from the phosphate rock, these species finally change into $Pb(OH)_2/Zn(OH)_2/Cu(OH)_2$ form, which is the most preferred tetrahedral coordination of lead, copper and zinc in aqueous solution [25] and makes it possible that surface complexation adsorption and co-precipitation occur during removal of Pb/Zn/Cu by phosphate rock.

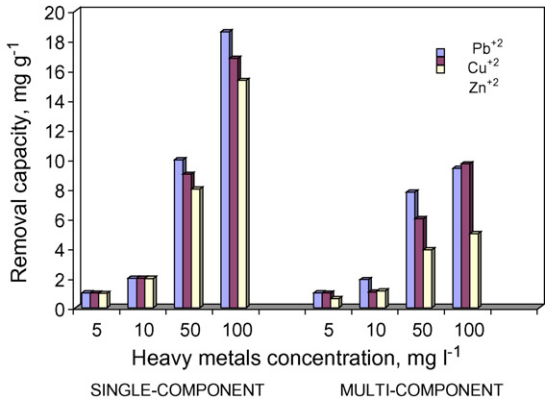

Fig. 5. Comparison of removal capacities.

Simultaneously, it appears that cation substitution (ion-exchange) is taking place in the present studies of adsorption but it is more pre-dominant at lower concentration, i.e. at considerably higher pH of metal solution where more amount of adsorbent (rock phosphate) is available. It has also been found that removal of thorium from dilute solution (lower concentration) takes place mostly through ion-exchange [26]. However at higher concentration, hydrolysis of thorium ions occurs and thorium hydroxide precipitation becomes more dominant.

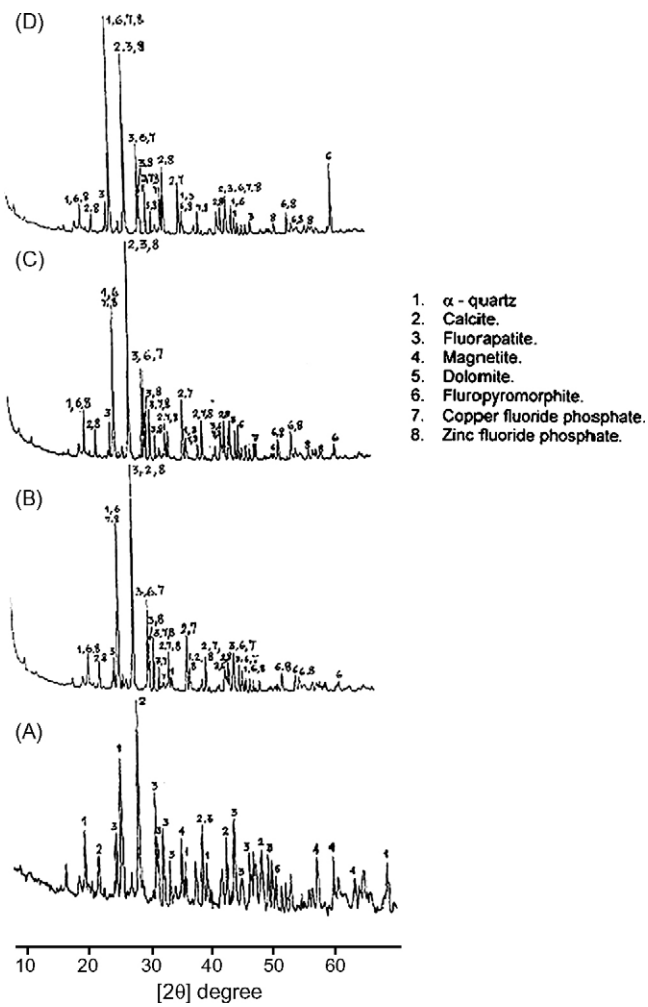

Fig. 6. X-ray diffraction patterns of phosphate rock (A) before treatment, (B) 10 mg l^{-1}, (C) 50 mg l^{-1} and (D) 100 mg l^{-1} of mixed (Pb + Cu + Zn) heavy metal solution.

These results can be explained alternatively by a dissolution–precipitation mechanism. More rock phosphate dissolved at lower pH, i.e. at considerably higher metal concentrations, and thus there were more P reacting with Pb, Cu and Zn to form fluoropyromorphite/copper fluoride phosphate/hopeite, respectively, as shown by X-ray diffraction peaks in Fig. 6.

Hence, surface complexation/co-precipitation, ion-exchange and dissolution–precipitation may occur during the heavy metal removal by phosphate rock, while, in different pH conditions, pre-dominant mechanism is different.

It is for reader's kind information that used adsorbents have been converted into a value added product by utilizing innovative Zero-waste concept to solve the used adsorbents disposal problem and thus protecting the environment. The details of this process have been described elsewhere [27].

4. Conclusion

The following points can be summarized from the above studies:

I. In comparison to high grade rock phosphate and hydroxyapatite which are relatively much costlier and have major applications for fertilizer manufacture and biological purposes respectively, low grade rock phosphate which is considered presently as a waste, has been found a suitable adsorbent.
II. The adsorption capacity of low-grade phosphate rock decreases in multi-component system as compared to single component.
III. Ion-exchange coupled with complexation mechanism has been found as the most probable mechanism responsible for metals uptake by sorption process.

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