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Lead and Cadmium removal from aqueous solution using an industrial gypsum by-product

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Abstract

The valorization of gypsum (by-product of phosphoric acid production) into useful product seems to be of important interest. In this study, the adsorption of lead (II) and cadmium (II) in an aqueous solution using both commercial gypsum (CG) and industrial gypsum by-product (IG) as adsorbents, has been investigated. The use of highly-purity CG allows the understanding of the adsorption phenomenon. The use of an IG as received from an industrial site allows the evaluation of its reactivity compared to pure CG. The adsorption experiments were carried out at ambient conditions for 24 h and the pH was recorded along the reaction. FTIR analyses were performed in order to examine the modification in the sulfate bound arrangement in the case of use of lead and/or cadmium. The obtained results have shown that the retention capacity of lead (II) and cadmium (II) by IG was similar that those obtained in the case of CG. However, gypsum by-product may be used as an alternative material to remove heavy metals in wastewaters.

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Keywords: Keywords: Adsorption, gypsum, uptake capacity, competition

1. Introduction

The stream of heavy metals can be correlated to point and diffuse sources. Point sources are located in municipal landfills and sites of industrial waste disposal. On the other hand, diffuse sources target a large volume of groundwater through the use of fertilizers on the fields of agriculture and green spaces. The remediation of wastewater is becoming a primordial interest in the last years. Different reactive materials such as activated carbon, zero-valence iron (Fe^0) and calcite ($CaCO_3$) have been recognized for the treatment of ground and industrial wastewaters.

The gypsum is a by-product of the reaction between sulfuric acid and phosphate rocks to produce phosphoric acid (H_3PO_4), and has serious storage problem. Different routes of valorization of gypsum have been proposed. It can be added to cement and natural pozzolan, which can influence the workability, porosity and mechanical strength [1]. Its use for the removal of heavy metals is intensively studied. In the literature, many recent studies have shown the ability of gypsum to remove heavy metals such as Arsenic, Cadmium, Lead, Zinc, etc [2,3]. The studies published by RINAUDO et al. (1988)

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[4] have shown that the gypsum nucleation increases with increasing the cadmium concentration. The crystalline structure of gypsum, characterized by a perfect cleavage orientation (010), results in the circulation of water, leading to dissolution on the surface (010) [5]. The adsorption of cadmium by gypsum reveals that the affinity of Cd^{2+} to SO_4^{2-} at the crystal surface is not larger than for Cd^{2+} to SO_4^{2-} in the solution [6]. The cadmium adsorbs up on (120) faces [4]. Many applications of gypsum have retained attention such as its use to stabilize and enhance mechanical properties of soil, or its use as adsorbent which can be adsorb up the fertilizer phosphate in soil to transform in dicalcium phosphate (brushite), or its formulation with Portland cement and natural pozzolan to control the added water and freezing-thawing and the long-term durability performance [1,7,8].

The main purpose of this research was firstly to investigate the possibility of the use of industrial gypsum waste as a reactive sorbent material for the removal of Pb^{2+} and Cd^{2+} and secondly to evaluate the selectivity and competitiveness potential of Pb^{2+} and Cd^{2+} to be immobilized. The present study is oriented to the valorization of gypsum as permeable reactive barrier to groundwater remediation. Purely-commercial gypsum was used as reference for the comparison with the physicochemical properties and retention capacity of industrial by-product gypsum.

2. Material and methods

2.1. Characteristics of the calcium sulfates

The gypsum ($CaSO_4.2H_2O$) used in this work is an industrial by-products (industrial gypsum: IG) of the phosphoric acid (H_3PO_4) production from phosphate rock (PRAYON®, Belgium), and a commercial gypsum (CG) supplied by Fisher Scientific (purity of 99.62%). The IG was sieved to pass a 1mm and the large fraction discarded, and CG was used as received. True density of the solid was measured using a helium pycnometer (AccuPyc 1330 V2.04N). Surface specific areas were determined on a Micromeritics Gemini 2360 using BET-method. The measurements were performed by nitrogen absorption at liquid nitrogen temperature and then desorption (adsorption gas N_2, heating temperature 150°C). The particle size (d_{50}) was 27.74 and 56.91µm of IG and CG respectively as determined by granulometric analysis performed on MALVERN Laser Mastersizer Hydro 2000. The chemical composition of used materials was obtained by ICP-AES technique, performed on a ULTIMA-2 (JOBIN YVON HORIBA. Before analysis, the sample was mineralized according to the French standard procedure NF X31-151 [9] which consists to the complete dissolution of solid particles by a mixture of concentrated HCl and HNO_3 acids. Mass titrations were carried out by suspending amount of material in 50 ml of KNO_3 0.01M electrolyte solution under N_2 atmosphere at lab temperature. The pH measurements were done after equilibration and pH_{PZC} values of IG and CG were evaluated by plotting the pH as a function of the added amount of material. **Table 1** summarizes the physicochemical properties of both IG and CG and **Fig. 1** shows the mass titration curves of IG and CG. The presence of functional groups in the different materials was performed by infrared spectroscopy using SHIMADZU FTIR (Fourier Transformed Infrared)-8400S spectrometer (**Fig. 2**).

Table 1: Physico-chemical characteristics of both IG and CG.

	IG	CG
True density ρ(g.cm^{-3})	2.25±0.00	2.25±0.00
Specific surface area S_{SA}(m².g^{-1})	26.27±0.35	21.83±0.18
Granulometric fraction (%)		
Sand	79.6	44.3
Silt	18.7	53.2
Clay	1.7	2.5
Chemical elements (mg.kg^{-1})		
Ca	487	—
Cd	9	—
P	10	<20
Pb	6	<4
SO_4	1925	—
pH	8.44±0.13	6.00±0.10
pH_{PZC}	8.35±0.01	8.61±0.01

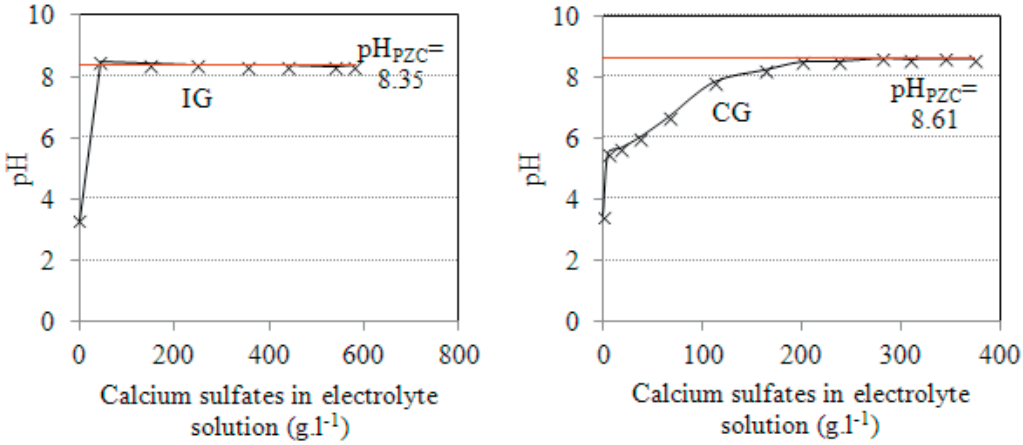

Fig. 1. The pH as a function of the added amount of IG and CG (KNO_3 0.01M as supporting electrolyte).

Both IG and CG had the similar true density and specific surface area. The IG particles are negatively charged (pH > pH_{PZC}) while CG particles are positively charged (pH < pH_{PZC}). The difference in surface charge can be due to the impurities omnipresent in IG that influences on surface charge. The classification and identification of materials following the geotechnical designation reveals that IG seems to have a sandy-silt texture and CG is identified as silty.

2.1. Reagents

$Pb(NO_3)_2$ and $Cd(NO_3)_2,2H_2O$ were supplied by Fisher Scientific and ACROS ORGANICS, respectively. Lead(II) and cadmium(II) aqueous solutions were obtained by dissolving nitrate salts in de-ionized water. Two kinds of solution were prepared, which were either single-metal (Pb^{2+} or Cd^{2+}) or multi-metals (Pb^{2+} and Cd^{2+}) with initial concentration of 6000ppm and 3258ppm of Pb^{2+} and Cd^{2+} respectively. The pH of initial aqueous solutions was determined.

2.3. Batch adsorption experiments

Batch adsorption experiments were conducted using prepared aqueous solution and adsorbent (IG and CG) with L/S ratio of 10. The adsorption was kept for 24 hours at the controlled temperature of 25±0.5°C under stirring rate of 350rpm. The pH and temperature were monitored automatically throughout the experiment.

Kinetic reaction was evaluated by sequential sampling procedure at 1min, 3min, 5min, 10min, 30min, 60min, 2h, 3h, 4h, 22h, 23h and at 24h. The volume of sample withdrawn from the reactor was about 5ml of suspension. Thereafter, the samples were filtered on a 0.45µm filter-paper and the transparent liquid was collected into 30 ml bottle containing 5 ml of HNO_3 (5%) to avoid any precipitation and de-ionized water. The chemical analyses were performed on filtered samples using ICP-AES (for soluble lead, cadmium, calcium and sulfur). The amount of Pb(II) and Cd(II) adsorbed (q_e) on either CG and IG ($mg.g^{-1}$) was calculated by using the equation as follows:

$$q_e = \frac{(C_0 - C_e)V}{W}$$

Where C_0 and C_e are the initial and equilibrium concentrations of Pb(II) and Cd(II) ions in the solution, respectively ($mg.L^{-1}$), V is the volume of solution (L) and W is the weight of the adsorbent (g).

3. Results and discussion

3.1. Characterization

Fig. 2 shows the results of FTIR analysis of the adsorbents before and after reaction. The water in both CG and IG is detected at 1620 and 1680 cm^{-1} and 3350, 3397 and 3516 cm^{-1}. The first region is explained by the presence of deformation modes of shear type which indicates the existence of two types of water molecules, loosely held water molecules at 1680 cm^{-1} and strongly held water molecules at 1620 cm^{-1} [10]. Consequently, water molecules in calcium sulfates are asymmetric. In the other side, spectral region between 1600 and 1800 cm^{-1} indicates H—O—H bending vibration. The sulfate group determines the symmetry with respect to the water molecules and is a high symmetry tetrahedral structure. In the case of IG and CG, sulfate peak is detected at 1105 cm^{-1}. The absorption band is symmetric stretching band (ν_3). Peaks at 600 and 667 cm^{-1} of CG and IG, respectively, are assigned to the bending vibrations (ν_4). The difference between the two intensities indicates that the symmetry is weakened by bounds with the water molecules. The disappearance of loosely held water molecules in the case of doped sample may be explained by the heating of samples at 105°C during 24 h.

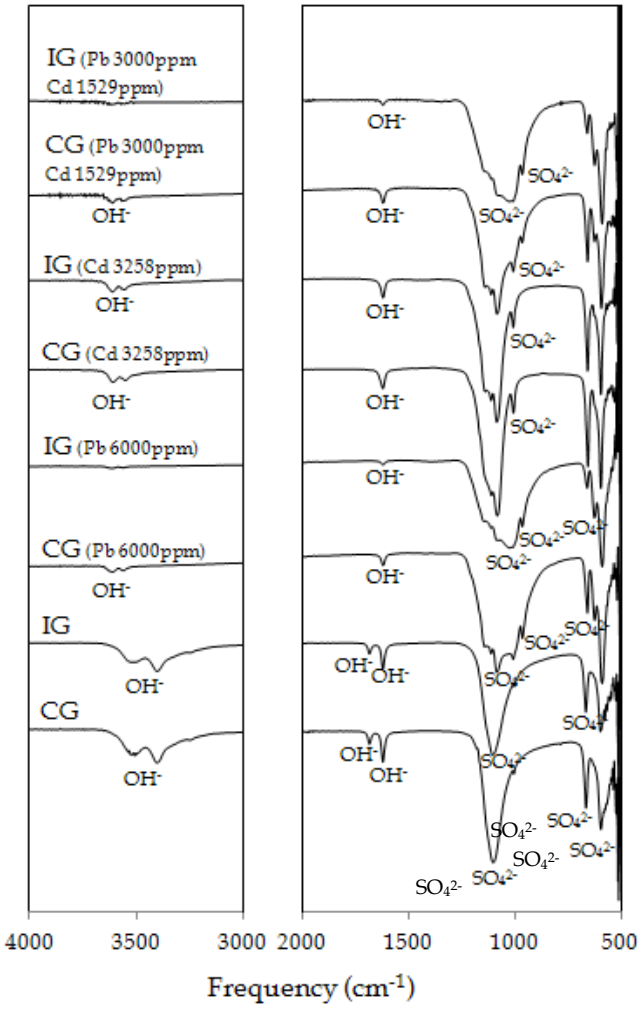

Fig. 2. Infrared spectra of IG and CG before and after adsorption of heavy metals.

A decrease in the intensities of sulfate bands located at 667 cm^{-1} and the apparition of band at 652 cm^{-1} were observed for both CG and IG doped with lead (6000 ppm). The apparition of shoulder bands at different intensities indicates the formation of new compounds and the modification of gypsum crystalline structure. The insertion of lead on the surface of gypsum particles led to the modification of characteristic absorption band of sulfate groups around 1100 cm^{-1}. The same result was observed in the case of gypsum doped with the multi-metals solution containing both lead (3000 ppm) and cadmium (1529 ppm). Concerning the samples doped with cadmium (3258 ppm), the apparition of shoulder band located at 1120 cm^{-1} indicates no further modification in structure of both CG and IG.

3.2. Adsorption isotherms

The results of adsorption experiments in batch reactors concerning the interaction of CG and IG with lead (6000 ppm) and cadmium (3258 ppm) are illustrated in **Fig. 3**.

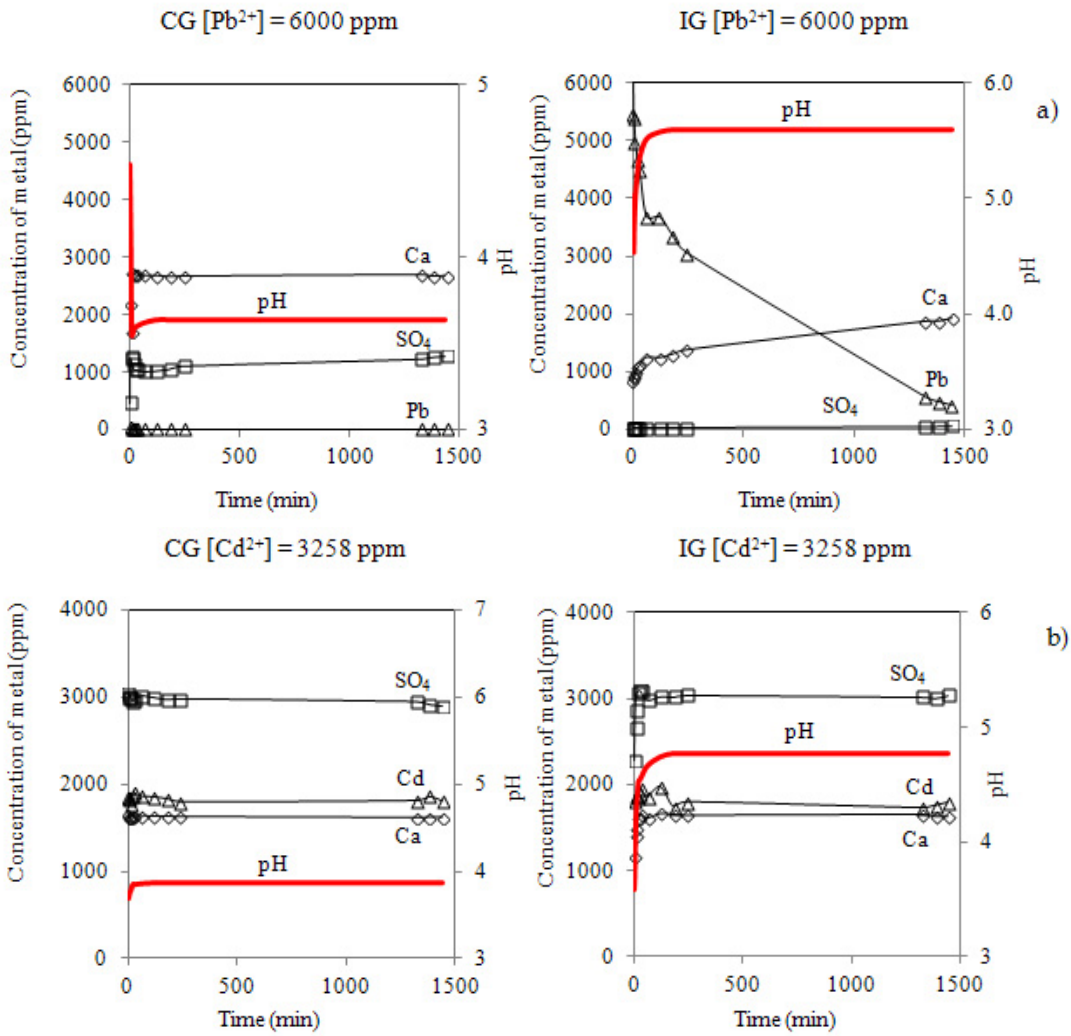

Fig. 3. Evolution of Ca, S, Pb and Cd concentrations as a function of time during the contact of CG and IG with Pb and Cd solutions. a) $[Pb_{aq}]_{initial}$ = 6000 ppm; b) $[Cd_{aq}]_{initial}$ = 3258 ppm.

Using CG, the equilibrium was estimated after 24 h of contact time. The lead (6000ppm) uptake was rapid in the first 1 min of contact in the case of CG. The concentration of Pb remained at low amount (≈ 14 $mg.L^{-1}$) after 10 min of contact time, which corresponded probably to the equilibrium with the solid state of lead. More than 99% of the Pb was removed from solution in this case. The initial pH of lead solution containing 6000 ppm Pb^{2+} was 4.9. The addition of CG to this solution led to a decrease of pH which was 3.6 at equilibrium. This may be explained by the high acidity of CG suspension and the competition between H^+ and Pb(II) ions for the adsorption. The increase of calcium and sulfate concentrations was explained by the dissolution of gypsum particles in acidic aqueous solution of lead nitrate. Beyond the 10 min contact time, the concentration of calcium and sulfate seemed to be stable.

When IG was used for the removal of lead (6000ppm), the Pb^{2+} concentration decreased dramatically down to about 150 ppm after 24h of reaction time. Otherwise, the concentration of SO_4^{2-} remained constant during the interaction time. The adsorption was considered as the main mechanism although surface precipitation could also occur [11]. The initial pH value of 4.5 for solution containing 6000ppm of Pb^{2+} increased slightly during the first interaction time, and reached a constant value of 5.6. This may be due to the formation of anglesite ($PbSO_4$), and the release of Ca^{2+} which is more basic than Pb^{2+}, as previously found by Astilleros et al (2010) [12].

The pH in the fixation of Cd was also monitored. The initial pH of Cd^{2+} solution (3258 ppm) was 3.7. After introducing CG, it increased slightly to 3.9, while the addition of IG to Cd solution led to the increase in pH value that reached 4.8 at the equilibrium.

The solubility product of CG was maintained constant during the interaction experiment ($Ks_{(CG)} = 1.2\times10^{-3}$). The concentration of Cd was reduced about 44% after the first contact of gypsum particles with the initial solution of cadmium (3258 ppm). This concentration remained constant preventing that the equilibrium was reached in the first minutes of contact time. The solubility product of IG decreased. Then, it was maintained constant after 5 minutes of the interaction experiment ($Ks_{(IG)} = 1.3\times10^{-3}$). The decrease of $Ks_{(IG)}$ may be due to the dissolution effect of IG and the supersaturation of solution with respect to cadmium sulfate formation. The formation of cadmium sulfate was attributed to the adsorption mechanism. Removal percentage of Cd(II) by IG was 46% at the equilibrium. The equilibrium was achieved after 3 hours of interaction period. In both cases, the stabilization in Cd concentration in the solution indicated that the gypsum particle surface was totally saturated by cadmium. **Table 2** gathers the values of adsorption capacities of both CG and IG. For both metals, the adsorption capacities of CG and IG were close to each other indicating that IG can be expected for the treatment of these metals in wastewaters.

Table 2: Adsorption capacities of commercial and industrial gypsum.

Adsorption capacity ($mg.g^{-1}$)	CG	IG
$[Pb^{2+}]$ = 6000 $mg.L^{-1}$	594±0	550±7
$[Cd^{2+}]$ = 3258 $mg.L^{-1}$	144±3	150±3

3.3. Competitive adsorption of multi-metals solution

The reactivity of CG and IG in the treatment of the solution containing simultaneously lead (II) and cadmium (II) was also investigated. A multi-metals solution containing 3000 ppm of Pb^{2+} and 1629 ppm of Cd was used for these experiments. This corresponds to the same molar concentration of the single-metal solutions, presented above. The results of adsorption were illustrated in **Fig. 4**. **Table 3** presents the removal percentage of both Pb(II) and Cd(II).

Table 3: Percentage of removed Pb and Cd in the adsorption of a multi-metals solution using CG and IG

	Removal percentage (%)	
Multi-metals solution	CG	IG
$[Pb_{aq}]$ = 3000 ppm	100	100
$[Cd_{aq}]$ = 1629 ppm	2	6

For both adsorbents, the results were similar to each other for the profiles of the concentration of all ions in the solution, including remained Pb^{2+} and Cd^{2+}; and released Ca^{2+} and SO_4^{2-}. The increase in concentrations of both Ca^{2+} and SO_4^{2-} was explained by the dissolution of gypsum and the crystallization of anglesite phase ($PbSO_4$). Then, the concentrations of Ca^{2+} and SO_4^{2-} were rapidly remained constant after some minutes of interaction time. For both adsorbent, lead was totally removed from the solution (**Table 3**). However, most of Cd remained in the solution after a long reaction time of 24 h and only 2-6% of Cd was removed. So the presence of lead reduced the adsorption of Cd on gypsum surface. The selectivity of adsorption may be correlated to the exchange affinity and to lead and cadmium hydrated radius (Pb^{2+}: 0.12 nm) and Cd^{2+}: 0.097 nm). Thus, lead is preferentially adsorbed on the surface of gypsum particles, which forms a layer of lead on the surface of adsorbent. This layer prevents the contact of Cd with active site of gypsum.

The pH of suspension increased as a function of reaction time and achieved a constant value at 6.1. The increase in the pH value indicated the beginning of the precipitation.

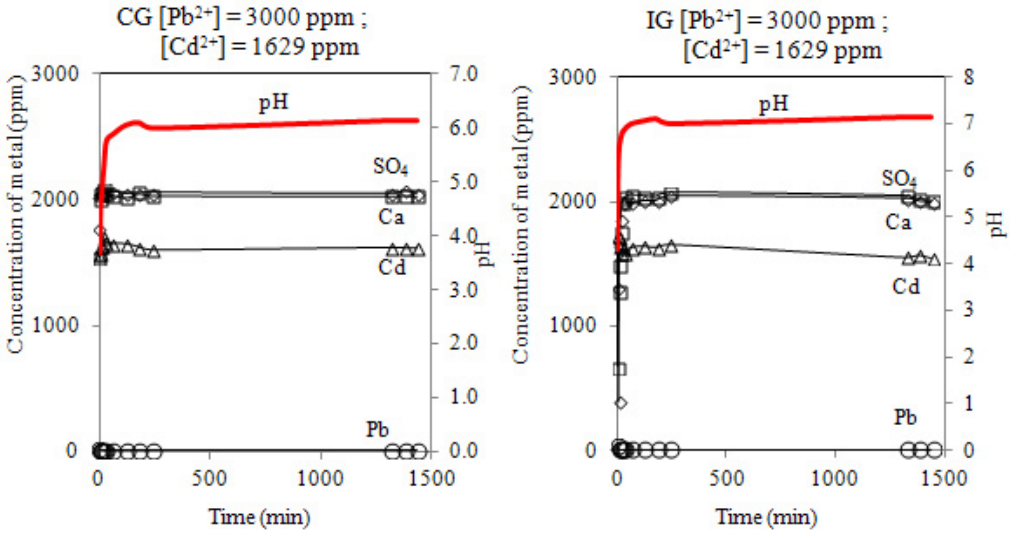

Fig. 4. Evolution of Ca, S, Pb and Cd concentrations as a function of time during the interaction of CG and IG with multi-metals Pb-Cd-solution ($[Pb_{aq}]_{initial}$ = 3000 ppm and $[Cd_{aq}]_{initial}$ = 1629 ppm) (SO_4 —□—; Ca —◊—; Cd —Δ—; Pb —○—).

4. Conclusions

The findings from this study are summarized as follows:

For a single-metal solution, both IG and CG showed the comparable reactivity in the adsorption of Cd(II) and Pb(II) in an aqueous solution. The uptake capacity of Pb(II) and Cd(II) reached about 550 and 145 $mg.g^{-1}$, respectively.

For a multi-metals solution containing simultaneously Cd(II) and Pb(II), Pb(II) was preferentially adsorbed on both CG and IG. The competition between Pb(II) and Cd(II) may be explained by the exchange affinity and hydrated radius of these heavy metals.

The obtained results showed that industrial by-product gypsum (IG) had a high reactivity for the removal of either Pb(II) or Cd(II) from an aqueous solution. This opens new route for its valorization as an alternative adsorbent in the decontamination of wastewater.

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Highlights:

The use of gypsum waste as an alternative adsorbent to treat wastewater leads to its valorisation and then reduces the treatment costs. The interaction of both lead (Pb^{2+}) and cadmium (Cd^{2+}) with gypsum waste and/or pure gypsum is presented here. A comparison of gypsum waste to pure gypsum regarding the adsorption capacity is proposed in this work.