



# BIOSORPTIVE-FLOTATION OF $Pb^{2+}$ AND $Cd^{2+}$ FROM WATER USING EGGSHELLS AS SORBENT AND OLEIC ACID AS SURFACTANT

S. E. Samra,<sup>[a]</sup> A. M. El-Nokrashy,<sup>[b]</sup> and A. A. El-Asmy<sup>[a,c]\*</sup>

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The removal and recovery of  $Pb^{2+}$  and  $Cd^{2+}$  is important for environmental protection and economic reasons. A new method, sorptive flotation, for the removal of  $Pb^{2+}$  and  $Cd^{2+}$  from aqueous solutions and water samples using eggshells as sorbent and oleic acid (HOL) as surfactant has been investigated. The process parameters (solution pH, initial concentration of metal ions, sorbent dose, shaking time, oleic acid (HOL) concentration, and temperature) on the flotation of  $Pb^{2+}$  and  $Cd^{2+}$  were studied in batch system. Under the optimum experimental conditions suggested, the removal of ~ 100 % of  $Pb^{2+}$  and  $Cd^{2+}$  was attained. The procedure was successfully applied for the removal of  $Pb^{2+}$  and  $Cd^{2+}$  from different natural water samples.

\* Corresponding Authors

Tel.: +96566734989:

E-Mail: aelasmy@yahoo.com

[a] Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt.

[b] Central Laboratory of drinking water, Dakahliya Company for Water & Wastewater, Mansoura, Egypt.

[c] Chemistry Department, Faculty of Science, Kuwait University, Kuwait.

## Introduction

Toxic heavy metals such as cadmium and lead are released into the environment. They are environmental pollutants due to strong tendency to concentrate in environment and in food chains.<sup>1-5</sup>

Heavy metal contamination exists in aqueous waste streams of metal plating facilities, mining operations and tanning, metal finishing industries, chemical and battery manufacturing, paints and metal extraction.<sup>5-7</sup> Wastewaters from chemical industry polluted by heavy metal ions represent a hazard for all living organisms especially for human.<sup>8,9</sup> These metals can cause danger for ecosystems and human health if they are discharged into natural water resources and may pose finally a serious health hazard.<sup>10-12</sup> As these toxic metals accumulate by living organisms, they produced diseases and disorders.<sup>13</sup>

Lead is one of the major pollutants because of its presence in automobile fuel and subsequent emission into the atmosphere in the exhaust gases.<sup>14,15</sup>  $Pb(II)$  is very toxic, causing many health problems to human such as: nausea, renal disturbances ending with renal failure hepatitis, encephalopathy, anemia, lung inefficiency, bone lesions, hypertension, cancer, nervous disorder, coma, convulsions and subtle effects on metabolism, intelligence and sickness even death.<sup>14,17</sup> Due to toxic effects of lead ions, its removal from waters and wastewaters is important in terms of protection of public health and environment.<sup>18,19</sup>

Also, cadmium is one of the heavy metals with a greatest potential hazard to humans and environment. It makes a way to water bodies through wastewater from metal plating industries, industries of Cd-Ni batteries, phosphate fertilizer, lead-zinc mining, pigments, stabilizers, ceramics, photograph development, textile printing industries and alloys.<sup>20,21</sup> The poisoning of cadmium in human causes high blood pressure, kidney damage, destruction of testicular tissue and red blood cells. In small amounts, cadmium is associated with hypertensive diseases and considered as carcinogenic to men.<sup>20</sup>

One of the cheap and easily available materials having great sorption for heavy metals is eggshells. Due to its high calcium content, eggshells usually have no commercial importance. Disposal of eggshells is also a serious problem for egg processing industries due to stricter environmental regulations and high landfill costs.<sup>22</sup> It is proposed to apply hen eggshells as low-cost biological sorbent of metal ions. In USA annually 120,000 tons of waste eggshells is generated and disposed in landfills.<sup>23,24</sup> The hen eggshells consists of mammillary matrix (i.e., eggshell membrane) consisting of interwoven protein fibers and spherical masses, and spongy matrix (i.e., calcified eggshell) made of calcium carbonate.<sup>25,26</sup>

The by-product eggshell weighs approximately 10 % of the total mass (~ 60 g) of hen egg,<sup>27</sup> representing a significant waste from the egg-derived products processor because it was traditionally useless and commonly disposed of in landfills without any pretreatment.<sup>26</sup> The chemical composition (by weight) of byproduct eggshell is calcium carbonate (94 %), magnesium carbonate (1 %), calcium phosphate (1 %) and organic matter (4 %).<sup>27,28</sup>

The sorptive-flotation process is variant for the adsorbing colloid flotation process and employs particles as sorbing material for the pollutants. Sorptive-flotation resembles oxide flotation activation by metal ions, sulfides depression by anions and coal flotation with oil. The sorbent may be minerals, polymeric resins, activated carbon, powdered marble wastes, by-products, biomass or microorganisms and

must have a high surface area, high reactivity with the pollutants to be removed and good characteristics of coagulation/flocculation and flotation.<sup>29-31</sup>

## Experimental

### Chemicals and solutions

Unless otherwise stated, all chemical reagents used in this study were of analytical grade.

### Surfactant preparation

Oleic acid (HOL) stock solution ( $6.36 \times 10^2 \text{ mol L}^{-1}$ ) was prepared from the food grade with sp.gr, 0.895 (provided from J.T. Baker chemical Co.) by dispersing 20 ml of oleic acid in one liter of kerosene. Further dilution was prepared as required for another concentration.

### $Pb^{2+}$ and $Cd^{2+}$ stock solutions

Stock solution ( $1000 \pm 2 \text{ mg L}^{-1}$ ) was prepared from Merck CRM (Germany)  $Pb(NO_3)_2$  or  $Cd(NO_3)_2$ , respectively, in  $HNO_3$ . The working solutions were made by diluting with deionized water. Standard aqueous solutions of  $HNO_3$  and/or NaOH were used for controlling the pH.

### Eggshells (ES)

The eggshells were obtained from eggshells processing markets. The sample was washed, dried for 2 h in an oven maintained at  $125^\circ\text{C}$  allowed to cool to room temperature and crushed. The sample sieved with size (25–63  $\mu\text{m}$ ) and stored in a desiccator. The functional groups of ES were characterized through IR spectra. The observable bands at 710, 875, 1420, 1797 and 2516  $\text{cm}^{-1}$  coincide with pure  $CaCO_3$ .<sup>25</sup> The chemical analysis of the sample was found to be  $CaCO_3$  (94 %),  $MgCO_3$  (1 %),  $Ca_3(PO_4)_2$  (1 %) and organic matter (4 %) as previously mentioned.<sup>27,28</sup>

### Apparatus

Atomic Absorption Spectrometer (AAS)-Varian AA240FS, Australian, was used for the determination of lead and cadmium concentrations at 217 and 228 nm respectively, provided with micro burette 5 and 10 ml. The infrared analysis was undertaken via a Mattson 5000 FT-IR Spectrophotometer and using KBr disc. The X-ray diffraction was recorded *via* a XRD Bruker, Germany. The scan electron microscope analysis was undertaken *via* SEM-JEO/JSMS 410, Japan with energy dispersive X-ray EDX Unit, Oxford, England. The pH was measured using a Symphony pH meter, USA, provided with a glass electrode. Also, Milli-Q A10/ Elix Millipore-deionizer, France was used for deionized water, Binder FD240-drying oven, Germany. The flotation cell was a cylindrical tube of 1.5 cm inner diameter and 29 cm length with a stopcock at the bottom and a quick-fit stopper at the top.

## Procedures

To study the different parameters affecting the sorptive-flotation process, 10 ml aliquot of suspension containing defined amounts of metal ions, sorbent sample, HCl or  $HNO_3$  and/or NaOH (for controlling pH) was introduced into a flotation cell. The flotation cell was shaken for the optimized time, to ensure complete flotation of metal ions with sorbent. To this suspension inside the cell, 2 ml of HOL was added. Again, the cell was inverted upside down many times by hand and kept standing for 5 min to complete flotation.

The flotation efficiency ( $R_e$  %) of metal ion was calculated from the following relation:

$$R_e = 100 \frac{(C_i - C_f)}{C_i}$$

where

$C_i$  and  $C_f$  denote the initial and final concentrations, respectively.

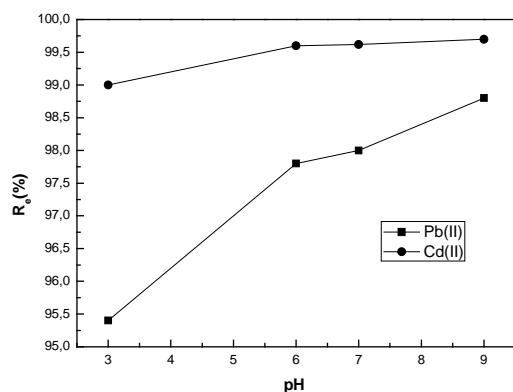
## Results and Discussion

### Effect of pH

As a function of solution pH, Pb and Cd species may exist as soluble  $Pb^{2+}$ , hydroxo-species  $[Pb(OH)^+]$ ,  $[Pb(OH)_3^-]$  or  $[Pb(OH)_4]^{2-}$  in addition to insoluble lead hydroxide,  $Pb(OH)_2$ , and hydrolytic species,  $Cd(OH)^+$ .<sup>32,33</sup>

The tendency of hydroxyl species in the float is sensitive to the solution pH. In order to find the optimal pH value for the sorptive-flotation process, the removal efficiency of  $Pb^{2+}$  and  $Cd^{2+}$  at pH 3, 6, 7 and 9 was studied. Figure 1 shows the effect of pH on the sorption-flotation for the removal  $10 \text{ mg L}^{-1} M^{2+}$  using 0.3 g ES and  $5 \times 10^{-2} \text{ mol L}^{-1}$  HOL.

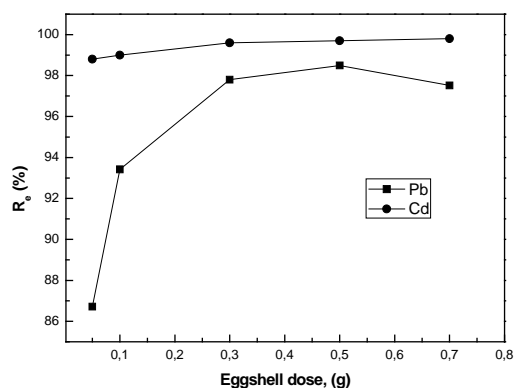
It should be noted that the removal of  $Pb^{2+}$  and  $Cd^{2+}$  increases with pH reaching ~ 100 % at pH 6–9 due to the adsorption of hydrolytic species in the same manner as that reported<sup>34</sup> and/or surface precipitation of the metal as insoluble carbonate, forming successive layers on the sorbent surface,<sup>35</sup> the predominant species at this pH range and the negatively charged surface of eggshells and precipitation of metal carbonate on ES surface. The aggregates of ES- $M^{2+}$  precipitate, being made hydrophobic by combination with undissociated oleic acid through hydrogen bonding and/or chemically with oleate anions. These hydrophobic aggregates are floated to the solution surface. Therefore, pH 6 was recommended throughout all other experiments. At  $\text{pH} < 6$ , the hydrolytic species of  $M^{2+}$  may adsorb or ion exchange with calcium sites of the ES sorbent. The adsorbent-adsorbate system is hydrophobic by combining with undissociated oleic acid molecules. Such combination may occur through hydrogen bonding of the hydroxide group of HOL.



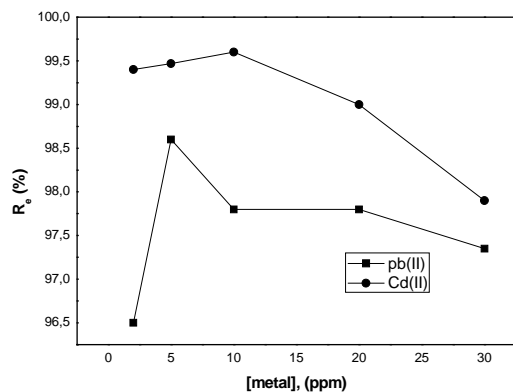
**Figure 1.** Removal of  $10 \text{ mg L}^{-1}$  metal ions on  $0.3 \text{ g}$  ES at different pH and  $5 \text{ min}$  shaking time.

### Effect of ES and $M^{2+}$ concentrations

Series of experiments were performed to study the influence of the eggshell dose (Figure 2) and changing the  $M^{2+}$  concentrations (Figure 3) on the removal percentage of  $Pb^{2+}$  and  $Cd^{2+}$  from aqueous solutions at pH 6 using  $5 \times 10^{-2} \text{ mol L}^{-1}$  HOL. As the concentration of  $M^{2+}$  increases, the removal % of the  $M^{2+}$  ions on ES increases.



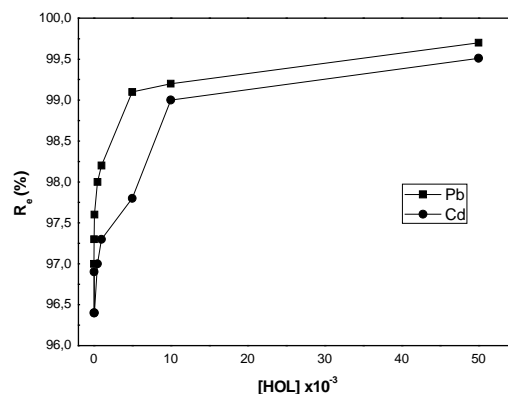
**Figure 2.** Removal % of  $10 \text{ mg L}^{-1} M^{2+}$  using different concentrations of ES and  $5 \times 10^{-2} \text{ mol L}^{-1}$  HOL at pH 6 and  $4 \text{ min}$  shaking time



**Figure 3.** Removal % of different concentrations of  $M^{2+}$  using  $0.3 \text{ g}$  ES and  $5 \times 10^{-2} \text{ mol L}^{-1}$  HOL at pH 6

### Effect of HOL concentration

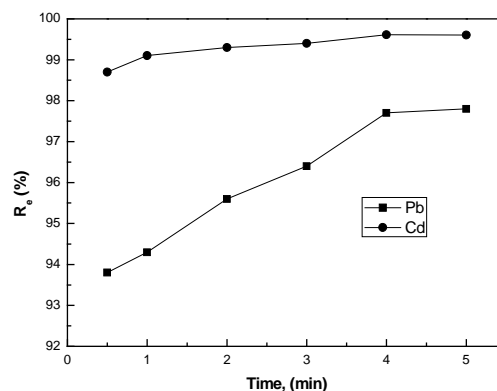
Series of experiments was undertaken to float  $10 \text{ mg L}^{-1} M^{2+}$  from aqueous solution at pH 6 in presence of  $0.3 \text{ g}$  of ES using different concentrations of HOL. The obtained results (Figure 4) showed that a maximum removal of  $M^{2+}$  ( $\sim 100\%$ ) was attained over HOL concentration of  $5 \times 10^{-2} \text{ mol L}^{-1}$ . Consequently, the concentration of HOL employed was fixed at  $5 \times 10^{-2} \text{ mol L}^{-1}$  throughout the study.



**Figure 4.** Removal % of  $10 \text{ mg L}^{-1} M^{2+}$  using  $0.3 \text{ g}$  ES and different concentrations of HOL at pH 6

### Effect of shaking time

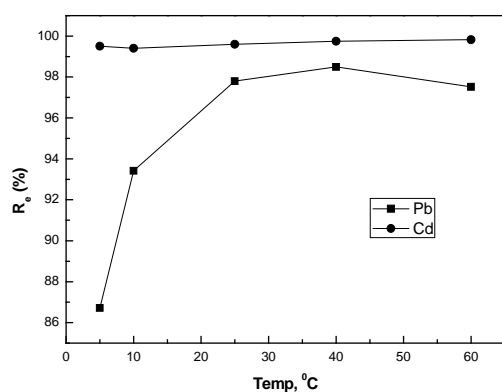
The % removal of  $M^{2+}$  with shaking time was studied using  $10 \text{ mg L}^{-1} M^{2+}$ ,  $0.3 \text{ g}$  ES and  $5 \times 10^{-2} \text{ mol L}^{-1}$  of HOL at pH 6. The shaking time was varied from  $0.5$  to  $5 \text{ min}$ . The obtained results (Figure 5) showed that the % removal increases to  $\sim 100\%$  after  $4 \text{ min}$  for  $10 \text{ mg L}^{-1} M^{2+}$ . Therefore,  $4 \text{ min}$  shaking was considered sufficient for the adsorption and flotation of  $M^{2+}$  having a concentration of  $10 \text{ mg L}^{-1}$  at pH 6.



**Figure 5.** Removal % of  $10 \text{ mg L}^{-1} M^{2+}$  using  $0.3 \text{ g}$  ES and  $5 \times 10^{-2} \text{ mol L}^{-1}$  HOL at different shaking time

### Effect of temperature

Solutions of definite pH containing  $10 \text{ mg L}^{-1} M^{2+}$  and  $0.3 \text{ g}$  of ES and another solution containing  $5 \times 10^{-2} \text{ mol L}^{-1}$  HOL were either heated or cooled. The surfactant solution was quickly poured onto the  $M^{2+}$  solution in the flotation cell. The mixture was then floated using the previous procedure. The obtained results (Figure 6) indicate that the % removal of  $M^{2+}$  increases as the temperature increases. Such data proposed that the adsorption of  $Pb^{2+}$  and  $Cd^{2+}$  may proceed through chemical-bond formation and ion exchange. Moreover, the increase of temperature to  $60^\circ\text{C}$  resulted in an increase in the rate of  $M^{2+}$  removing for the same dose of ES sorbent,  $0.3 \text{ g}$ . Such results suggest the creation of new active sites on ES surface available for adsorption of  $M^{2+}$ .



**Figure 6.** The removal of  $10 \text{ mg L}^{-1}$  metal ions using  $0.3 \text{ g}$  of ES and  $5 \times 10^{-2} \text{ mol L}^{-1}$  HOL at different Temperature.

### Application

The recommended procedure was performed to recover  $10 \text{ mg L}^{-1} M^{2+}$  added to aqueous and some natural water samples. The sorptive-flotation experiments were carried out using  $10 \text{ ml}$  of sample solutions with its initial pH. The obtained results (Table 1) show that the recovery is satisfactory.

**Table 1.** Recovery of  $10 \text{ mg L}^{-1}$  metal ions added to some water samples using  $0.3 \text{ g}$  of ES sorbent and  $5 \times 10^{-2} \text{ mol L}^{-1}$ .

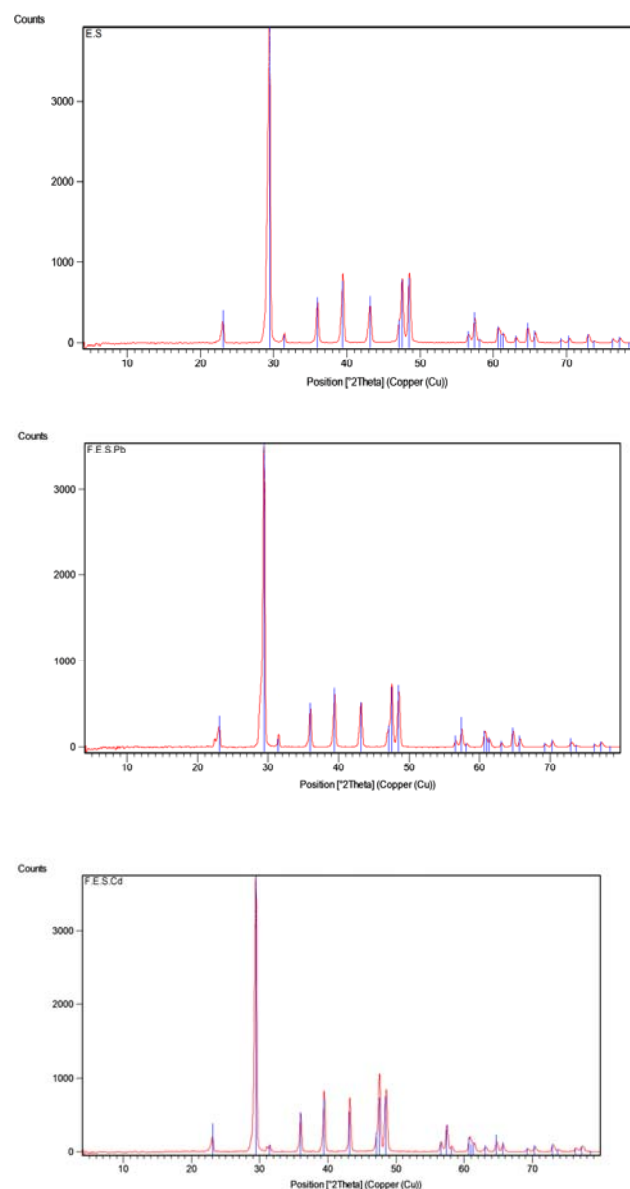
Sample (location)	Found ( $\text{mg L}^{-1}$ )		$R_c$ %	
	Pb(II)	Cd(II)	Pb(II)	Cd(II)
Distilled water	9.95	9.961	99.50	99.61
Tap water (our laboratory)	9.87	9.846	98.70	98.46
Nile water (Mansoura City)	9.92	9.910	99.20	99.10
Underground water (Mansoura City)	9.89	9.786	98.90	97.86
Sea water (Sharm El-Sheikh)	9.78	9.698	97.80	96.98

### Instrumental studies

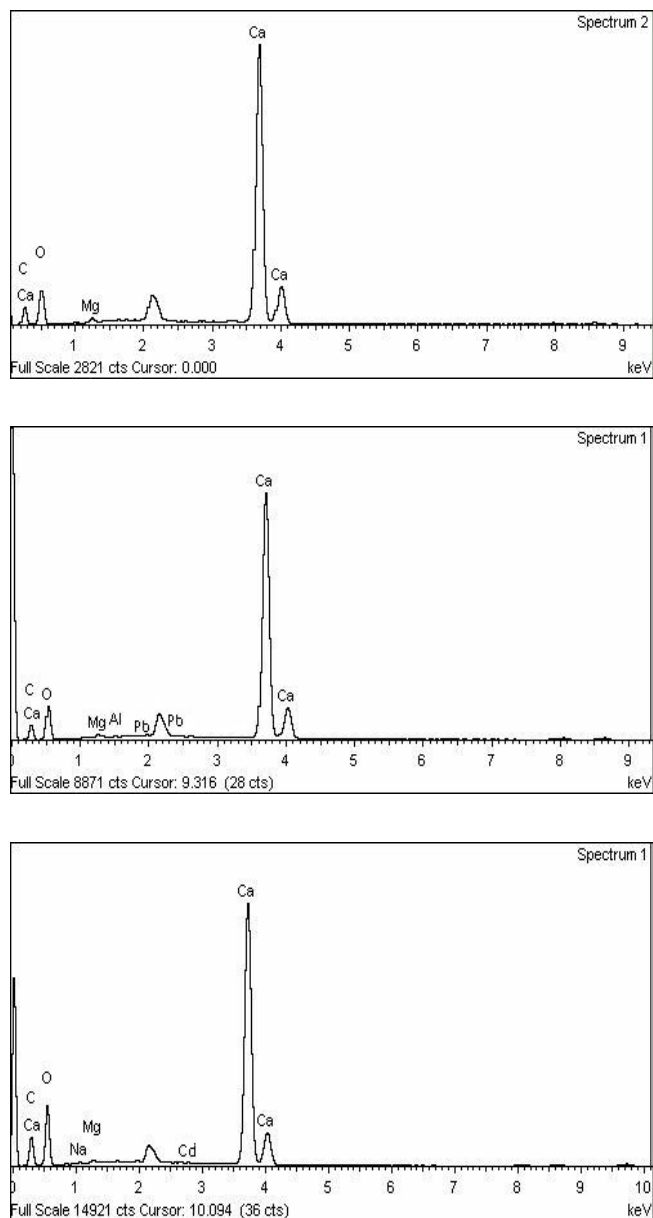
The  $Pb^{2+}$  and  $Cd^{2+}$  sorption by ES is interpreted by XRD, EDX and SEM analyses. Powered XRD studies help in understanding the changes occurred on the structure of ES sorption. XRD data (Figures 7a-7c) provided clear evidence of modification in the surface morphologies in form of cleavage.

In the EDX graph (Figures 8a-8c), the presence of  $Pb^{2+}$  and  $Cd^{2+}$  after treatment is observed. The SEM image of ES before and after metal ions adsorption (Figures 9a-9c) is corresponding to the morphological changes in the surface of the adsorbents in the coverage of pores of the ES due to the adsorption of  $Pb^{2+}$  and  $Cd^{2+}$ .

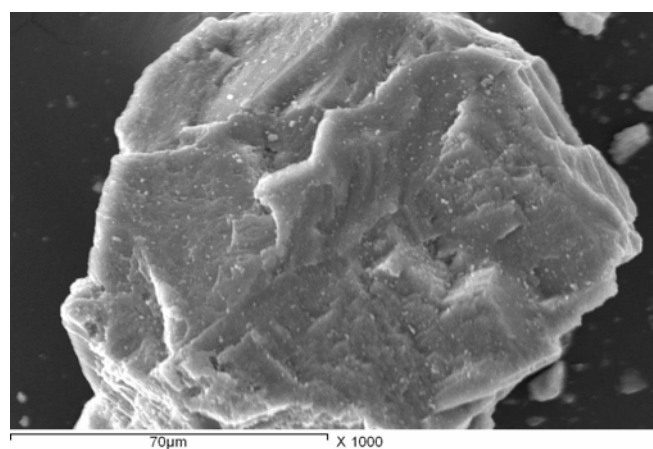
(a)



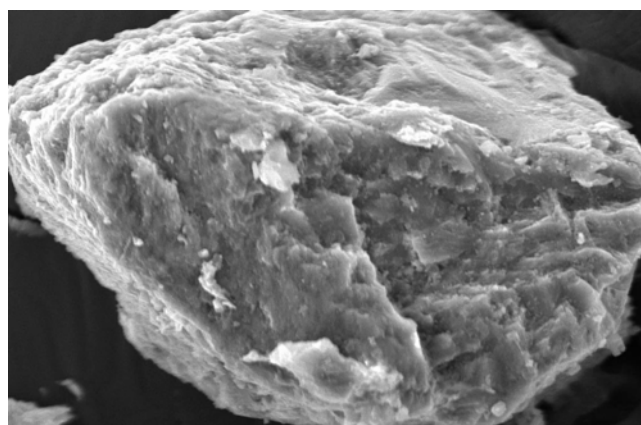
**Figure 7.** XRD of ES (a) before flotation; (b) after flotation with  $Pb^{2+}$  (c) after flotation with  $Cd^{2+}$ .



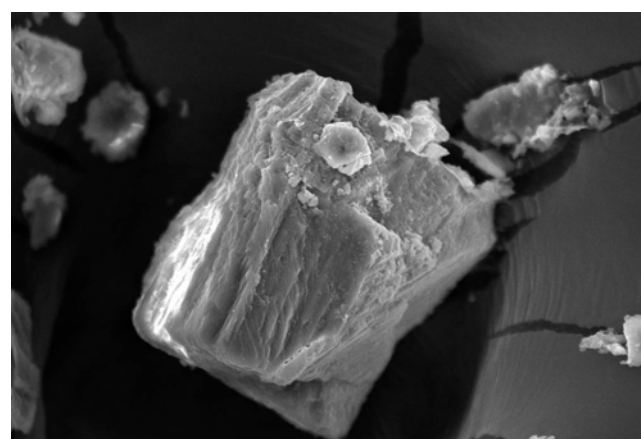
**Figure 8.** EDX of ES (a) before flotation; (b); after flotation with  $Pb^{2+}$  (c) after flotation with  $Cd^{2+}$ .



(a)



(b)



(c)

**Figure 9.** SEM of ES (a) before flotation; (b); after flotation with  $Pb^{2+}$  (c) after flotation with  $Cd^{2+}$ .

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