



### CONVERTING LOW GRADE SOLID WASTES INTO USEFUL PRODUCTS

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**Abstract.** Utilization of solid wastes attracts the researcher's attention because it solves the environmental pollution problems, save the disposal costs and produce useful products that can generate profit. In this project, Jordanian Low Grade Phosphates (JLGP) waste and Immobilized Jordanian Low Grade Phosphates (IJLGP) particles were used to remove cobalt heavy metal from waste water effluent. The effect of pH, time, adsorption amount, concentration of cobalt, and particle size were investigated for both adsorbents. This study showed that the JLGP has high adsorption capacity towards the removal of cobalt ions from aqueous solutions. Results showed that the adsorption of cobalt ions onto JLGP increased as the amount of adsorbent, the surface area, the equilibrium pH and the ion concentration increase. On the other hand, results showed that the adsorption of immobilized low-grade phosphate waste was more efficient than that for non-immobilized waste.

## 1 INTRODUCTION

One of the most aquatic pollutants due to the rapid increase in industrialization activities is the heavy metals pollution. Enhanced industrial activities during recent decades has led to the discharge of unprecedented volume of wastewater, which is a serious cause of environmental degradation. Heavy metals, due to their high toxicity, pose a serious threat to biota and environment. The presence of heavy metals in the environment is of major concern because of their extreme toxicity and tendency for bioaccumulation in the food chain even in relative low concentrations [1]. Heavy metals pollute the environment from various industries such as metal plating, electroplating, mixing and metallurgical process, ceramic, batteries, pigment manufacturing, plastic manufacturing and textile [2].

Due to their health and toxicological effects, environmental agencies and authorities have set strict regulations to maintain the limit of heavy metals in wastewater below the maximum acceptable concentration levels. These strict regulations accelerated the research for new technologies which are environment friendly and can reduce heavy metals concentrations in the discharged wastewaters to be below the maximum allowable limits. The conventional methods used to remove heavy metals from wastewaters include chemical solvent extraction, chemical precipitation, ion exchange, and adsorption.

As cobalt is widely dispersed in the environment humans may be exposed to it by breathing air, drinking water and eating food that contains cobalt. Skin contact with soil or water that contains cobalt may also enhance exposure. Cobalt is not often freely available in the environment, but when cobalt particles are not bound to soil or sediment particles, the uptake by plants and animals is higher and accumulation in plants and animals may occur [3].

Immobilization is an attractive technique to fix and retain JLGP on suitable natural or synthetic materials support for range of physical and chemical unit operations [4]. Immobilization of the JLGP in solid matrix structures creates a material with the right size, mechanical strength, rigidity and porosity necessary for use in unit operations typical of chemical engineering [5].

The main advantages of this technique include:

High JLGP concentrations

Combination of high JLGP concentrations and high flow rates allows high volumetric productivities.



- Easy separation from mixture
- Increased stability of JLGP
- Increase mechanical strength of JLGP.

The objectives of this work is to investigate the technical feasibility of using Jordanian Low Grade Phosphate (JLGP) for the removal of cobalt ions from the aqueous solutions without any chemical treatment and compared that with the immobilized JLGP. The effects of pH, agitation time, amount of adsorbent and cobalt initial concentration on the adsorption uptake will be studied for both cases.

## 2 EXPERIMENTAL PROCEDURE

### 2.1 Preparation of adsorbent

The adsorbent used in this study was Jordanian Low Grade Phosphate (JLGP). Table 1 lists the physical and chemical characteristics of this material [6]. The samples used in this study were collected from the rejected waste area of the Jordan Phosphate Mines at Al-Hasa city. These samples were sieved to different particle sizes (from 0.063 mm to 2 mm) prior to use. As a sedimentary phosphate the used material contained calcite, organic matter, quartz and clay.

Chemical Analysis		Physical Analysis	
Component	Composition, %	Property	Value
P <sub>2</sub> O <sub>5</sub>	33.8	Moisture	1.21%
CaO	50.5	Bulk density	1.175 g/ml
SO <sub>2</sub>	1.15		
SiO <sub>2</sub>	6.1		
CO <sub>2</sub>	3.42		
F	3.74		
Al <sub>2</sub> O <sub>3</sub>	0.93		
Fe <sub>2</sub> O <sub>3</sub>	0.26		
MgO	0.25		
Na <sub>2</sub> O	0.545		
CaO/P <sub>2</sub> O <sub>5</sub>	1.49		

Table 1: Physical and chemical analysis of JLGP

### 2.2 Preparation of stock solution

The adsorbate stock solution of 1000 mg/l Co<sup>2+</sup> was prepared from Cobalt acetate tetrahydrate (C<sub>4</sub>H<sub>6</sub>CoO<sub>4</sub>.4H<sub>2</sub>O) in distilled water. Experimental solution of the desired concentrations were obtained by successive dilutions to obtain concentrations ranging from 20-200 mg/l Co<sup>2+</sup>.

### 2.3 Analytical Instruments

- pH meter (Thermo Orion, 420) has been used for pH determination of the cobalt solution.
- Verian Atomic Absorption (Spectra AA, 880) spectrophotometer has been used to measure the concentration of cobalt.
- Reciprocating shaker



### 2.4 2.4. Preparation of Immobilized JLGP

Immobilized JLGP was prepared by entrapping powdered of JLGP with 0.063 mm diameter in an alginate matrix produced by ionic polymerization in calcium chloride solution, according to the following procedures [4]. The powdered JLGP was suspended in a 2% sodium alginate (BDH, UK) solution kept at a temperature of 60 °C. The mixture was then dropped into a 2% calcium chloride (BDH, UK) solution using a peristaltic pump. The drops of Na-alginate solution gelled into  $3.5 \pm 0.1$  mm diameter beads upon contact with calcium chloride solution (Figure 1). The beads were washed well and then rinsed in deionized water and stored at 4 °C.

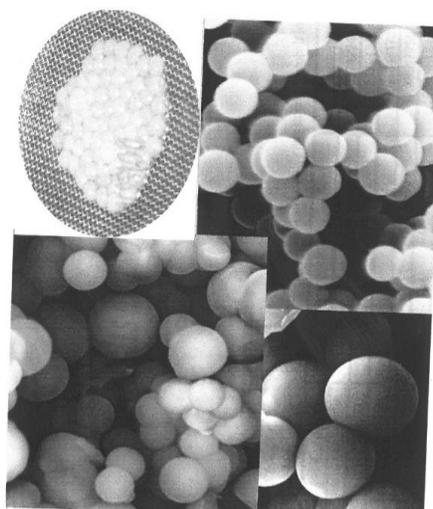


Figure 1: An immobilized Jordanian Low Grade Phosphate (IJLGP)



### 3 RESULTS AND DISCUSSIONS

#### 3.1 Effect of percentage removal of cobalt

After determining the optimum parameters for cobalt ions removal such as equilibrium pH at 4, equilibrium time at 30 minutes, optimum particle size at 0.063 mm, and optimum adsorbent mass at 0.1 g, the percentage removal was studied for JLGP without immobilization for different  $\text{Co}^{2+}$  from 20-200 ppm as a function of time. Figure 2 shows that a contact time of 30 minutes was sufficient to achieve equilibrium and the percentage removal increased with increasing the initial  $\text{Co}^{2+}$  concentration. This is due to the increase in the active sites for adsorption but reaches a point where no significant removal was observed because the adsorbent reach the saturation limit and there were no more active sites for adsorption.

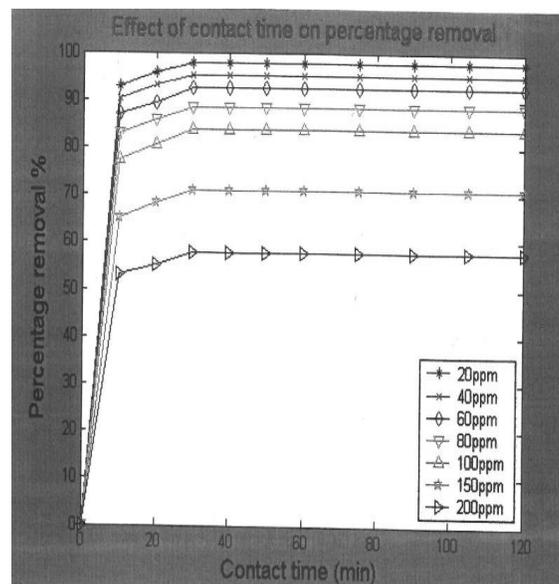


Figure 2: Percentage removal of  $\text{Co}^{2+}$  on Jordanian Low Grade Phosphate (JLGP)

at temperature 25 °C, pH 4, JLGP mas 0.069 g and particle size 0.063 mm.



### 3.2 Effects of percentage removal using Immobilized JLGP

The effect of time at 100 ppm  $\text{Co}^{2+}$  on the percentage removal on the JLGP with and without immobilization was studied as shown in Figure 3.

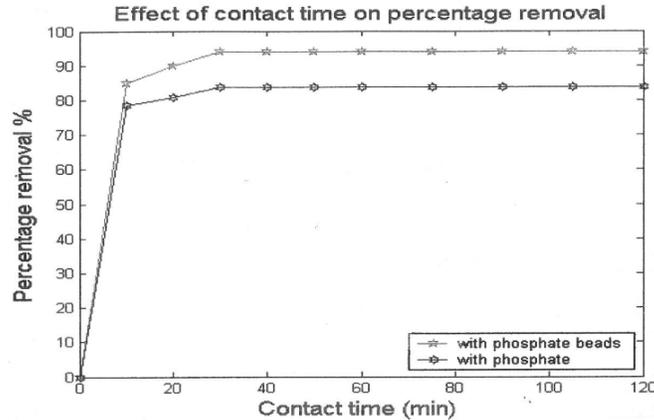


Figure 3: Percentage removal of  $\text{Co}^{2+}$  on JLGP and IJLGP

at temperature 25 °C, pH 4, JLGP mas 0.069 g and particle size 0.063 mm.

Alginic acid or alginate, the salt of alginic acid, is the common name given to the family of linear polysaccharides containing 1,4-linked  $\beta$ -D-manuronic (M) and  $\alpha$ -L-guluronic (G) acid residues arranged in a nonregular, block wise order along the chain [6]. Alginates were preferred over other materials because of their various advantages such as biodegradability, hydrophilic properties, presence of carboxylic group, and natural origin. In the present work, Ca-alginate in the bead form was used as an adsorbent and a support material for entrapment of JLGP then used for the removal of  $\text{Co}^{2+}$  from aqueous solution. Alginate beads were prepared by cross-linking with divalent calcium ions, and alginate droplets were precipitated in the bead form (diameter about  $3.5 \pm 0.1$  mm) in calcium chloride solution. The effect of using these beads in adsorption process when the initial cobalt ions equal 100 ppm was studied. The results show that the percentage removal by using these beads is greater than those with normal phosphate and the equilibrium time is the same. This might be due to an increase in the surface area for adsorption then increase in the metal binding sites.

### 3.3 Kinetic Studies

Also kinetic models were used to test the experimental data. The kinetics of the adsorption data was analyzed using two kinetic models, first order and pseudo-second order kinetic model. These models correlate solute uptake, which are important in predicting the reactor volume. The parameters of these two models were in Table 2. It is clear that there are differences between the parameters when using immobilized phosphates compare to non-immobilized phosphate but both show an agreement in the adsorption kinetics as pseudo-second order kinetics.



System	First order kinetics		
	Rate constant k (min <sup>-1</sup> )	q <sub>e</sub> (mg/g)	R <sup>2</sup>
Co with phosphate	0.17	40.45	0.868
Co with phosphate beads	0.054	40.45	0.364
Pseudo-second order kinetics			
Rate constant k (g/mg.min)	q <sub>e</sub> (mg/g)	h (mg/g.min)	R <sup>2</sup>
0.054	58.82	185.19	0.98
0.033	66.67	147.06	0.98

Table 2: Kinetic parameters for the adsorption of Co<sup>2+</sup> on JLGP with and without immobilization

#### 4 CONCLUSIONS

In this study, it has been shown that JLGP has high adsorption capacity towards the removal of cobalt ions from aqueous solutions. Also this study shows that the adsorption efficiency of immobilized adsorbents was greater than the non-immobilized adsorbents because alginate beads increase in the surface area for adsorption then increase in the metal binding sites. The type of adsorption here is physical adsorption.

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