

# EFFECTS OF CONTACT TIME, INITIAL COBALT ION CONCENTRATION, PH, AND BIOSORBENT DOSAGE OF SURFACE ORANGE PEEL AND MAIZE AGRO-WASTE ADSORBENTS TO REMOVE COBALT FROM WATER

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## ABSTRACT

The ability of Co (II) removal from aqueous solution using natural cheap agro-waste such as orange peel and maize was investigated. The effects of pH, contact time, adsorbents dosage, and initial Co(II) concentration on the removal of cobalt have been studied. The biosorbents were characterized by FT-IR spectroscopy that confirmed physical adsorption of cobalt by adsorbents.

The maximum efficiencies of cobalt removal by orange peel and maize cob were 40% and 42 % respectively. The optimum parameter required for maximum adsorption determined as follows: pH =4-8 for orange peel and 8.0-8.5 for maize cob, contact time=15 minutes, adsorbents dosage=5 gm/L and cobalt concentration =25 mg/L.

**Keywords:** Orange peel, Maize cob, Adsorption, Cobalt ion, Removal efficiency.

## INTRODUCTION

Different industrial wastes to water environment caused a serious problem especially heavy metal accumulation which affected the characteristics of the resulted water with specific qualification and quantification of several important factors such as BOD. The main important health problem of heavy metal waste is their bio- accumulation with no chance to be changing to other less toxic inorganic or organic materials<sup>1</sup>.

This ecosystem problem is going to be increased with rapid rate in all over the world by direct way from industrial location processing or indirect from air and soil pollution. Water contamination issue is not only important to human life as public health considerations or other creators now but for the next generations on the earth plant<sup>2</sup>.

Heavy metal term is known as any metallic element with high density such as mercury, lead, nickel, cadmium, copper, cobalt, arsenic,...etc. with toxic properties ranged in part per million of concentration as a

classification of toxicity definition which can be presented in stream, rivers, lakes, or ground water with uncontrolled human actions<sup>3</sup>.

Different methods with physical and chemical specifications were achieved to deal with this public health concern such as separation, adsorption, plating, and others<sup>4-11</sup>. One of most applied and effective technique for this critical issue is adsorption with privilege of low cost compared with others<sup>7,8,10-12</sup>.

Variable materials had been used for adsorption process of organic and inorganic pollutants likewaste cooked tea, raw waste agriculture products such as rice husk, olivestone, garlic peel, sawdust, banana peel, carica papaya seed, date tree leave ....., or their activated carbon<sup>7, 11, 13-31</sup>.

Orange peel contains carbon, hydrogen, oxygen, and nitrogen atoms as main constituents in the back ground of cellulose, hemicellulose, lignin, pectin, and others besides forming the major functional groups that help in presence of binding sites for pollutants<sup>32, 33</sup>.

This work is aimed to use low cost adsorbents, which consist of maize cob and orange peel as plant wastes for removal of cobalt from water and study the effects of contact time, initial cobalt ion concentration, pH, and biosorbent dosage on the biosorption efficiency were also investigated.

## EXPERIMENTAL

### Reagents

1000 ppm cobalt stock solution was prepared by dissolving 2.0197 gm of cobalt chloride hexahydrate in 1 liter deionized water. Other concentrations were obtained by a proper dilution of stock solution. The pH solution was adjusted by adding dilute solutions of HCl and NaOH.

### APPARATUS

Atomic Absorption (Phoenix-986-AA Spectrophotometer, England), pH meter (inoLab, pH 7110, Germany), Centrifuge machine (ALL PROCORPORATION, 800 B CENTRIFUGE, India), and Shaker (Edmund Buhler D 7400 Tubingen KS 10, Germany) were used in this work.

### Preparation of adsorbents

Two cheap naturally available waste adsorbents orange peel and maize cob were repeatedly washed with deionized water in order to remove dust and other inorganic impurities, then oven dried at 100°C to reduce the moisture contents. After drying, the adsorbents were crushed and sieved. The particle sizes were (0.6 and 0.3) mm for orange peel and maize cob respectively were used.

### Study of process parameters

Effect of four parameters, cobalt ion concentration, contact time, pH and adsorbent dosage were studied. To study the effect of certain parameter changed progressively by keeping the other three constants.

### Batch adsorption studies

Batch adsorption experiments were carried out with 20 mL of cobalt solution. 0.1 gm of the previously prepared biosorbent was added to the solution. The mixture was shaken at 250 rpm at room temperature, after separation by centrifuge, the solution of cobalt was analyzed using atomic absorption spectrophotometer. The percent removal of Cobalt was calculated as follows:

$$\begin{aligned} \text{\% Removal of cobalt} \\ = [(C_i - C_e) / C_i] \times 100 \end{aligned}$$

Where  $C_i$  and  $C_e$  are the initial and final cobalt concentrations (ppm) respectively.

## RESULTS AND DISCUSSION

### Effect of pH

It is known in heavy metal adsorption studies that pH of the aqueous solution is an important controlling parameter<sup>34</sup> because of its direct relationship as a competition type of hydrogen ions with metal ions towards active sites on the biosorbent surface<sup>35</sup>. As the pH increased from 1.0 to 8.5, the biosorption efficiency of orange peel to remove cobalt increased from 8% to 40% (Figure 1). The maximum adsorption occurs at pH 4-8.

Figure 2 shows removal of cobalt at varying pH range by using maize cob as adsorbent where the maximum adsorption of cobalt ion was observed at pH 8-8.5. This result supports that the biosorption is pH dependent<sup>36</sup>.

As mentioned in introduction section, presence of polysaccharide, lipids, and/or protein in the cell wall of the agriculture waste enhances the physicochemical adsorption phenomenon by the specific influence of active functional group binding sites to metal ions<sup>11</sup>. The amount of adsorption increases with increasing pH up to the point >8.5 where the cobalt precipitate.

### Effect of contact time

The second fundamental indicator of adsorption success is studying of contact time to clarify this transfer phenomena retention capacity of the metallic pollutant under study. Figure 3 indicates a typical saturation curve where equilibrium was at 15 minutes for two adsorbents with no change of cobalt ion uptake after about 15 minutes<sup>11</sup>.

### Effect of adsorbents dosage

The third effective factor in cobalt bio-adsorption process was adsorbent dosage or weight which was varying from 1 gm/L to 50 gm/L as shown in Figure 4 that pointed the good removal efficiency of orange peel towards cobalt removal more than maize cob.

Figure 4 shows that the percent removal of cobalt raised with the increase in the amount of adsorbent with maximum removal of 40% and 20% of cobalt were obtained at 0.06 gm of orange peel and maize cob respectively which is sufficient for optimal removal of cobalt with no significant changing after this point.

### Effect of initial concentration of cobalt

Our studied factors were finished with the effect of initial concentration of the metallic cobalt ion solution as shown in Figure 5 with both adsorbents. It had more influence degree

with orange peel (40-34)% removal efficiency than maize cob (20-5)% at concentration range (25-200) mg/L.

### FTIR Spectroscopic analysis

Infrared technique was used for identification of functional groups responsible for metal uptake compared with absence of adsorption procedure was applied. The FTIR spectra of orange peel and maize cob (Figure 6) show a broad absorption peaks around  $3420\text{ cm}^{-1}$  belongs to hydroxyl groups of phenols and alcohols. Also, absorption bands (2924 and

$2900\text{ cm}^{-1}$  of C-H stretching vibration attributed to methyl, methylene and methoxy groups, and stretching vibrations of (1744 and  $1708\text{ cm}^{-1}$  due to non-ionic carboxyl groups and may be due to carboxylic acids or their esters in orange peel and maize cob respectively<sup>38, 39</sup>. The peaks (1644 and  $1636\text{ cm}^{-1}$  due to the C-C stretching were good indication to the aromatic C-C bond. These vibration values were lowered after bio-adsorption achieved with cobalt ion marking the physical adsorption occurrence in both adsorbents.

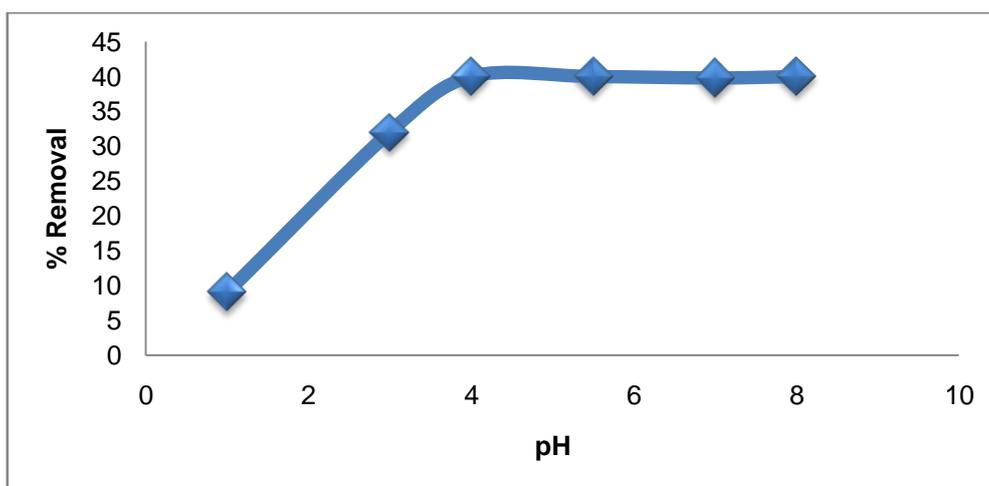


Fig. 1: Effect of pH on the removal of cobalt by orange peel [C<sub>0</sub>=25ppm, amount of adsorbent= 0.1gm, contact time= 60 min]

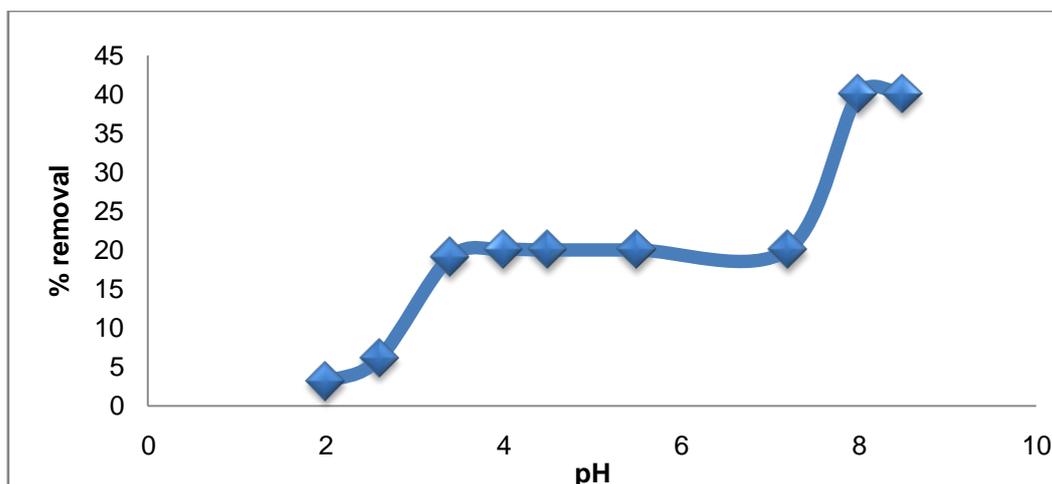
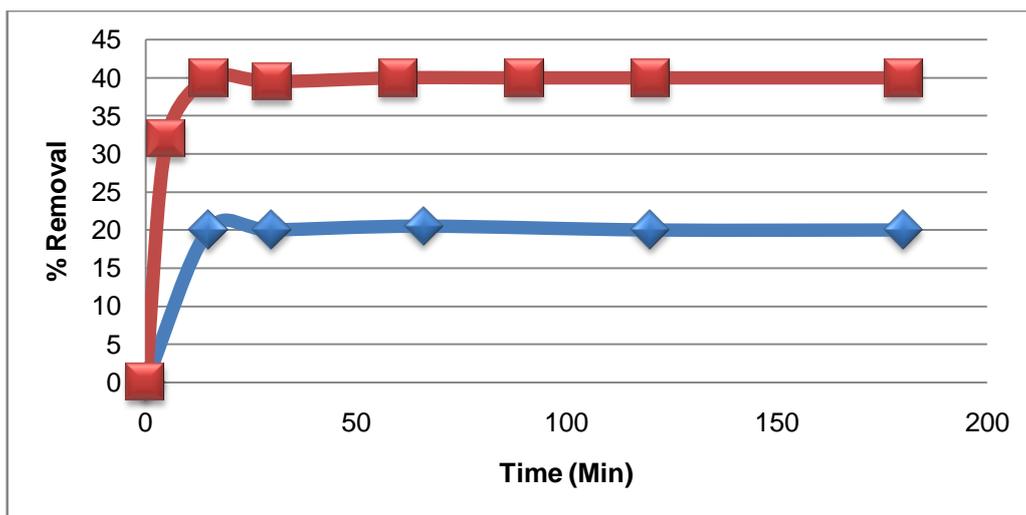
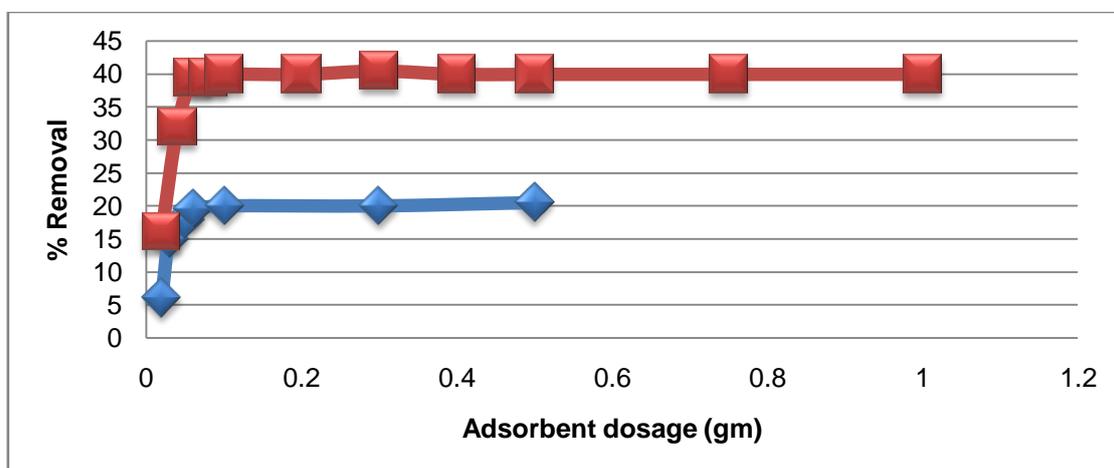


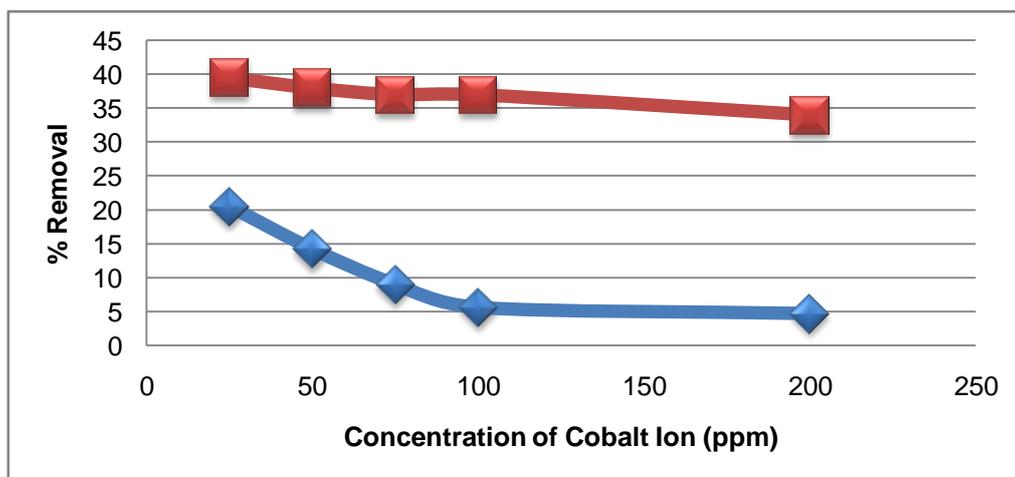
Fig. 2: Effect of pH on the removal of cobalt by maize cob [C<sub>0</sub>=25ppm, amount of adsorbent= 0.1gm, contact time= 60 min]



**Fig. 3: Effect of contact time on the removal of cobalt**  
 [ $C_0=25\text{ppm}$ ,  $\text{pH}= 5.5$ , amount of adsorbent= 0.1gm, orange peel (red), maize cob (blue)]



**Fig. 4: Effect of adsorbents on the removal of cobalt**  
 $C_0=25\text{ppm}$ ,  $\text{pH}= 5.5$ , orange peel (red), maize cob (blue)]



**Fig. 5: Effect of cobalt concentration on removal of cobalt**  
 $\text{pH}= 5.5$ , amount of adsorbent= 0.1gm, orange peel (red), maize cob (blue)]

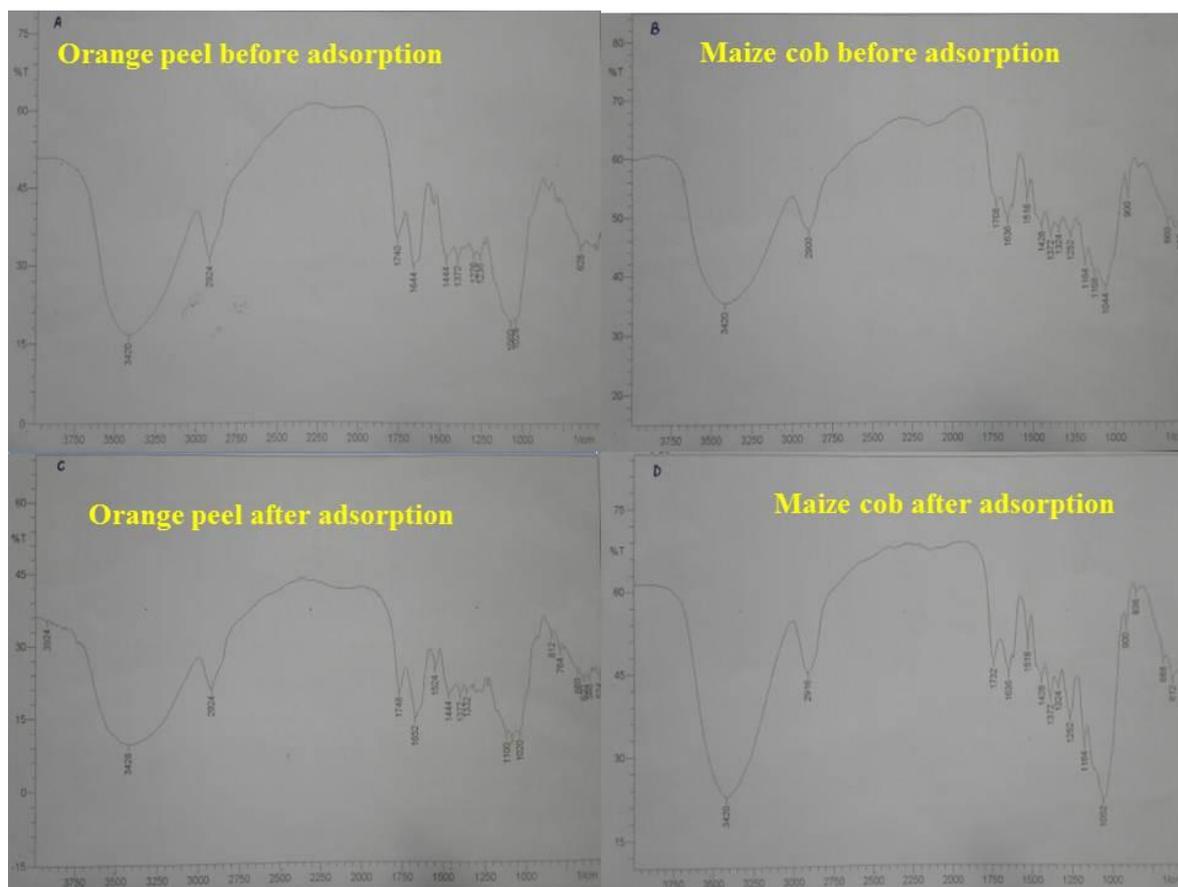


Fig. 6: FTIR spectra of orange peel and maize cob before and after adsorption of cobalt ion

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