# Reuse of Olive Cake as Low Cost Adsorbent to Eliminate Co (II) from Water Media

Mohamed Ackacha [1 +] and Massoda Farjallah [2]

[1] Faculty of Education, Sebha University P. O Box 5243, D' Njamena, Chad

[2] Chemistry Department, Faculty of Science, Sebha University P. O Box 625, Sebha, Libya

**Abstract.** In this study, the ability of olive cake to adsorb Co (II) from aqueous solutions was investigated in a batch experiments technique. The following parameters are constants: pH, 5; initial concentration of Co (II), 350 mg/l; shaking speed, 400 rpm and adsorbent dose, 0.2 g/l. The surface area ($S_{BET}$) of olive cake samples were determined from nitrogen adsorption data using multi-station high-speed gas sorption analyzer. A computer program was devised for determine the pore volume ($V_P$) of olive cake samples. The experimental equilibrium data were tested for the Langmuir isotherm model and they were fit well with model. The equilibrium adsorption capacities were 45, 49 and 153 mg/g at 303, 313 and 323 K, respectively. The desorbed Co (II) from olive cake samples was achieved using 0.2 M $HNO_3$ solution. The $CaCl_2$ (1 M) solution was used to regenerate the olive cake samples for reuse another time. The effect of temperature on mass lost of olive cake samples was studied. It was found that a 50 % mass lost of olive cake samples (0.4 to 0.2 g) after adsorption, desorption, regeneration and reuse processes. On the other hand, there is no much different on the mass lost after reuse process (cycle 2) was found (0.096-0.1 g) at different temperatures.

**Keywords:** Olive cake, Langmuir, isotherm.

## 1. Introduction

Cobalt, one of the common toxic metals affecting the water environment, is present in several industries such as electroplating, paints, miming, metallurgical and pigments [1]. Cobalt cause several health problems such as low blood pressure, lung irritation, paralysis and diarrhea [2]. The recommended levels of cobalt in drinking water recommended by different countries is 0.05 mg/l [3].

There are different techniques for reducing heavy metals from water environment including membrane filtration, ion exchange, chemical precipitation and liquid extraction [4]. Most of these techniques are take too much time and expensive or inefficient [5]. The adsorption technique is proved to be an effective and attractive process for reducing lead cations from water media. A low cost agricultures materials were used in literatures as adsorbents [6]. Among these materials, rice hull and sawdust [7], peanut shells [8], orange peel [9] and crab shells [10]. The basic composition of agriculture materials is probably lignin, hemicellulose and cellulose. These materials are contain hydroxyl and carboxyl functional groups which are promptly available to interact with cations [11].

Desorption can be carried out by proton exchange using acids, chelating agents such as EDTA or exchange with other ions (i.e. $CaCl_2$). An efficient eluent is one that desorbs the metal completely without deteriorating. In case of desorption of heavy metals from agriculture materials, $HNO_3$ was found as more effective than other inorganic acids such as HCl or $H_2SO_4$ [12].

---

[+] Corresponding author. Tel.: + (235 95390045).
  *E-mail address*: (ackacha57@yahoo.com).

After metal desorption, a regeneration step can be used to prevent a loss of biosorption capacity. The choice of regeneration agent depends on the kind of adsorbent used and metals adsorbed. In some cases, a simple wash with distilled water is sufficient as regeneration agent [13].

In this research, the ability of olive cake samples (OCS) as low cost adsorbent to reduce Co (II) from water environment has been studied using batch adsorption experiments. Desorption of Co (II) from OCS surface by treatment with nitric acid and regeneration of this adsorbent with calcium chloride were also studied. Finally, OCS were reused for anther adsorption process.

## 2. Materials and Methods

### 2.1. Biosorbent Material

OCS were collected from Gharian city, Libya. The collected samples were treated with acetone to remove the residual oil from them, washed several times with deionized water and dried in an oven at 100 $^{\circ}$C for two hours. The dried samples then grounded and very fine powder was obtained (particles size <125 μm). The obtained powder was kept in a desiccator for further use.

### 2.2. Preparation of Adsorbate

Stock standard solution of Co (II) (350 mg/l) was prepared from cobalt nitrate salt (Codex, Italy) after appropriate dilution with distilled water. The pH of the stock solution was established at 5 using dilute solutions of hydrochloric acid or sodium hydroxide.

### 2.3. Batch Experiments

Batch adsorption experiments were carried out by the use of a rotary Shaker (Stuart Scientific, UK) at 400 rpm/min in a 100 ml shaking flasks containing 100 ml of 350 mg/l Co (II) solutions. A doses of 0.02 g of OCS was added to the flasks. The contents of the flasks were shacked for desiarable time (15-120 minute). OCS were separated by filtration and dried in an oven at 100 $^{\circ}$C for two hours and stored in a desiccator for desorption and regeneration use. The concentrations of Co (II) were determined by titration with EDTA using xylenol orange as indicator [14].

The amount of adsorption at equilibrium, $q_e$ (mg/g) was computed as follows:

$$q_e = \frac{(C_o - C_{eq})V}{W} \tag{1}$$

where $C_o$ and $C_{eq}$ are the initial and equilibrium concentration of Co (II) (mg/l), V is the volume of solution (l), W is the weight of OCS (g).

### 2.4. Co (II) Desorption and Olive Cake Regeneration

The stored weighed of OCS (section 2.3.) were placed in contact with 0.2 M $HNO_3$ to desorbed Co (II) from them. The samples were filtered and repeatedly washed with deionized water after each desorption to eliminate the excess of acid and dried at 100 $^{\circ}$C for two hours.

In order to regenerate the OCS for farther use, The samples were soaked in 1 M $CaCl_2$ for 35 min, filtered and repeatedly washed with deionized water and dried at 100 $^{\circ}$C for two hours before being reused in a second sorption-desorption cycle.

After each biosorption at used temperature, the final adsorption capacity of Co (II) adsorbed ($Me_{ads}$, mg/g) was calculated with the following expression [15]:

$$Me_{ads} = (Me_0 + Me_{res}) - Me_f \tag{2}$$

where $Me_0$ is the initial amount of Co (II) in solution, (mg/g); $Me_{res}$ is the residual amount of Co (II) retained from the previous desorption, when applicable, (mg/g); $Me_f$ is the final amount of Co (II) in solution, mg/g.

### 2.5. Determination of Surface Area and Pore Volumes of OCS

The surface area of OCS ($S_{BET}$) were determined from nitrogen adsorption data using multi-station high-speed gas sorption analyzer, Nova 2200 (Quantachrome Corporation, USA). A computer program was devised for determine the pore volume ($V_P$) of OCS.

# 3. Results and Discussion

## 3.1. Isotherm Analysis

A well known isotherm model, Langmuir was applied for analysis of sorption data obtained at different contact time (15-120 minute) of Co (II), keeping the sorbent dose, concentration of Co (II) and pH constants at 0.2 g/l, 350 mg/l and 5, respectively. The isotherms were achieved at temperatures 303, 313 and 323 K. The Langmuir equation [16] valid for a monolayer of adsorbate onto a surface of adsorbent of identical sites, can be represents as

$$\frac{t}{q} = \frac{1}{Q_{max} \cdot b} + \frac{1}{Q_{max}} t \tag{3}$$

where Qmax (mg/g) and b (l/g) are the Langmuir constants showing the maximum amount of Co (II) adsorbed per unit weight of OCS and the energy of the adsorbent, respectivily.

Langmuir isotherm showed linear plot and values of Langmuir constant ($Q_{max}$ and b) calculated from the slop and intercept of the plot (Fig. 1) are presented in Table 1. The high values of linear coefficients ($R^2$) as shown in Table 1 proved that the present work is follow the Langmuir isotherm model.

The essential characteristics of Langmuir isotherm model can be explained in terms of equilibrium parameter ($R_L$) which is defined as

$$R_L = \frac{1}{1 + bC_0} \tag{4}$$

The values of $R_L$ indicates if the shape of isotherm is favorable ($0 \langle R_L \langle 1$) [17]. The values of $R_L$ were in the range (0.01-0.12) as shown in Table 1. This indicating the favorable of this work with Langmuir assumption.
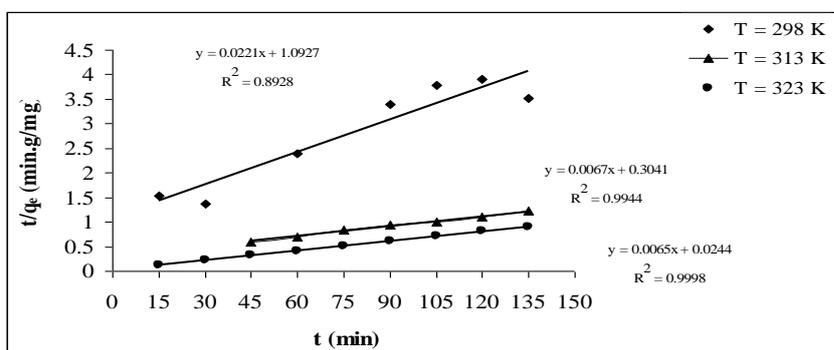


Fig. 1: Langmuir isotherm model for Co (II) sorption by OCS

Table 1: Langmuir isotherm model parameters for Co (II) sorption by OCS

| T (K) | $Q_{max}$ (mg/g) | $R_L$ | b (l/mg) | $R^2$ |
|---|---|---|---|---|
| 303 | 45 | 0.12 | 0.02 | 0.8928 |
| 313 | 49 | 0.01 | 0.02 | 0.9944 |
| 323 | 153 | 0.06 | 0.06 | 0.9998 |

## 3.2. Isotherm Analysis Adsorption, Desorption, Regeneration and Reuse Cycles at Different Temperatures

The Co (II) adsorption onto OCS and desorption of Co (II) from OCS are shown in Table 2. The regeneration and reuse of OCS are also displayed in Table 2. The amount of adsorption uptake increased after regeneration and reuse at different temperatures in cycle 1, for instance 87 increase to 408 mg/g at 303 K. On the other hand, the amount of adsorption capacity (cycle 2) after reuse step decrease from 408 to 286 mg/g at 303 K and from 343 to 333 mg/g at 323 K, indicating the favorable of high temperature in case of regenerate the OCS with CaCl$_2$. Therefore the process can be classified as endothermic due to the increase of the adsorption capacity of Co (II) onto OCS with increase temperature.

Table 2: Adsorption, desorption, regeneration and reuse cycles

| Temperature (T) | Stage | Cycle 1 $q_e$ (mg/g) | Cycle 2 $q_e$ (mg/g) |
|---|---|---|---|
| 303 | Adsorption | 87 | 73 |
| | Desorption | 167 | 164 |
| | Regeneration | 316 | 214 |
| | Reuse | 408 | 286 |
| 313 | Adsorption | 103 | 127 |
| | Desorption | 217 | 204 |
| | Regeneration | 339 | 206 |
| | Reuse | 342 | 332 |
| 323 | Adsorption | 148 | 134 |
| | Desorption | 263 | 195 |
| | Regeneration | 341 | 271 |
| | Reuse | 343 | 333 |

Table 3: The effect of temperature on mass lost of OCS

| Temperature (T) | Stage | Cycle 1 mass (g) | Cycle 2 mass (g) |
|---|---|---|---|
| 303 | Adsorption | 0.40 | 0.20 |
| | Desorption | 0.36 | 0.0.18 |
| | Regeneration | 0.28 | 0.13 |
| | Reuse | 0.20 | 0.10 |
| 313 | Adsorption | 0.40 | 0.20 |
| | Desorption | 0.37 | 0.19 |
| | Regeneration | 0.24 | 0.15 |
| | Reuse | 0.20 | 0.097 |
| 323 | Adsorption | 0.40 | 0.21 |
| | Desorption | 0.37 | 0.16 |
| | Regeneration | 0.26 | 0.12 |
| | Reuse | 0.20 | 0.096 |

## 3.3. Effect of Temperature on Mass Lost of OCS

The effect of contact temperature on the mass lost during the adsorption, desorption, regeneration and reuse processes are presented in Table 3. It is very clear from Table 3 that, there is a 50 % mass lost of OCS (0.4 to 0.2 g) after adsorption, desorption, regeneration and reuse processes. On the other hand, there is no much different on the mass lost after reuse process (cycle 2) was found (0.096-0.1 g) at different temperatures, this means there is a small effect of the temperatures on the mass lost of OCS after reuse process.

## 3.4. Determination of Surface Area and Pore Volume of OCS

Table 4 summarize surface area properties of the native OCS and OCS after desorption and regeneration steps obtained from the nitrogen adsorption isotherms such as the total, external and internal areas. The pore volume were also presented in Table 4. $S_{BET}$ for native OCS (550 $m^2$/g) is higher than OCS with adsorbed Co (II) (450 $m^2$/g). The $V_P$ reveal a decrease in contributions of both micro and meso-pores to the total volume of pores, thus the $V_P$ of native OCS (0.690 ml/g) whereas, the $V_P$ of OCS with adsorbed Co (II) (0.325 ml/g).

The treatment of OCS with $HNO_3$ enhanced change the surface functional groups (create new active sites) and also influenced the pores structures. In contrast, $S_{BET}$ for OCS after desorbed of Co (II) by $HNO_3$ was increased from 450 to 700 $m^2$/g and $V_P$ also increased from 0.325 to 0.790 ml/g, this indicates that, the

treatment of OCS with $HNO_3$ caused the changes in the adsorption capacity from 148 to 263 mg/g which lined to changes in surface chemistry and porosity.

Further treatment for regeneration the OCS with $CaCl_2$, causes the increasing of adsorption capacity from 263 to 341 mg/g due to the formation of new pores and hence increased each $S_{BET}$ from 700 to 900 $m^2$/g and $V_P$ from 0.790 to 0.855 ml/g.

Table 4: Nitrogen adsorption data obtained for OCS

| Sample | $S_{BET}$ ($m^2$/g) | $V_P$ (ml/g) | $q_e$ (mg/g) |
|---|---|---|---|
| Native OCS | 550 | 0.690 | - |
| OCS with adsorbed Co (II) | 450 | 0.325 | 148 |
| OCS after desorbed of Co (II) by $HNO_3$ | 700 | 0.790 | 263 |
| OCS after generation with $CaCl_2$ | 900 | 0.855 | 341 |

## 4. Conclusion

The present study indicated that OCS is an effective adsorbent for the removal of Co (II) from aqueous solutions. The maximum adsorption capacities of Co (II) on OCS were 45, 49 and 153 mg/g at 303, 313 and 323 K, respectively. The Langmuir isotherm model was used to interpret the adsorption phenomenon of the adsorbate, and the results implies that the surface was homogenous. The treatment of OCS with $HNO_3$ increased the adsorption capacity for Co (II) by increasing the $S_{BET}$ values. Using the $CaCl_2$ for regeneration enhanced the $S_{BET}$ values and the adsorption capacity of Co (II) on OCS.

Therfore, we are recommended the using of $HNO_3$ for activation and $CaC_2$ for regeneration, which are the conventionat techniques for development the adsorption capacity for our sample.

## 5. Acknowledgements

## 6. References

[1]  V Manohar, B Noeline, and T Amirudhan. Adsorption performance of Alpillared bentonite clay for the removal of cobalt (II) from aqueous phase. *Appl Clay Sci.* 2006; 31: 194-206.

[2]  A Ahmadpour, M Tahmasbi, T Rohani Bastami, and J Amel Besharati. Rapid removal of cobalt ion from aqueous solutions by almond green shell. *J Hazard Mater* 2009; 141: 925-930.

[3]  I Shibi, andT Anircudhan. Kinetic and equilibrum modeling of adsorption of cobalt (II) from aqueous solutions onto surface modified lignocellulosics (*Musa paradisiaca*). *India J Chemic Technol.* 2006; 13: 567-575.

[4]  H Lalhruaitluanga, K Jayaram, M Prasad, and K Kumar, Lead (II) adsorption from aqueous solutions by raw and activated charcoals of Melocanna baccifera Roxburgh (bamboo) – A comparative study. *J Hazard Mater* 2010; 175: 311-318.

[5]  Q Li, J Zhai, W Zhang, M Wang, andJ Zhou. Kinetic studies of adsorption of Pb (II), Cr (III) and Cu (II) fromaqueous solution by sawdust and modified peanut husk. *J Hazard Mater* 2006; 141: 163-167.

[6]  Y Jiang, H Pang, and B Liao. Removal of copper (II) ions from aqueous solution by modified bagasse. *J Hazard Mater* 2008; 164: 1-9.

[7]  F Qin, B Wen, X Shan, and Y Xie. Mechanisms of competitive adsorption of Pb, Cu and Cd om peat. *Environ Pollut* 2005; 144: 669-680.

[8]  F Asadi, H Shariatmadari, and N Mirghaffari. Modification of rice husk and sawdustsorptive characteristics for remove heavy metals from synthetic solutions and wastewater. *J Hazard Mater* 2007; 154: 451-458.

[9]  K Wilson, H Yang, C Seo, W Marshall. Select metal adsorption by activated made from peanut shells. *Bioresour Technol* 2005; 97: 2266-2270.

[10] X Li, Y Tang, X Cao, D Lu, F Luo, and W Shao. Preparation and evalution of orange peel cellulose adsorbents for

effecttive removal of cadmium, zinc, cobalt and nickel. *Colloid Surfac A*. 2007; 317: 512-521.

[11] D Kim. The removal by crab shell of mixed heavy metal ions in aqueous solutions. *Bioresour Technol* 2002; 87: 355-357.

[12] Y Mata, M Blazquez, A Ballester, and J Munoz. Sugar-beet pulp pectin gels as biosorbent for heavy metals: preparation and determination of biosorption and desorption characteristics. *Chemic Eng J*. 2009; 150: 289-301.

[13] K Sekhar, C Kamala, N Chary, A Sastry, T Rao, and M Vairamani. Removal of lead from aqueous solutions using an immobilized biomaterial derived from a plant biomass. *J Hazard Mater* 2004; 108: 111-117.

[14] M Sekar, and V Sakhi. Kinetics and equilibrium adsorption study of lead (II) on activated carbon prepared from cocount shell. *J Colloid Interface Sci*. 2004. 79: 307-313.

[15] Y Mata, M Biázquez, A Ballester, J González, and J Muñoz. Studies on sorption, desorption, regeneration and reuse of sugar-beet pectine gels for heavy metal removal. *J Hazard Mater* 2010; 178(1-3): 243-248.

[16] Y HO, and A Ofomaja. Biosorptionthermodynamics of cadmium on cocunt copra methods biosorbent. *Biochem Eng J* 2006; 30: 117-123.

[17] K Jayaram, and M prasad. Removal of Pb (II) from aqueous solution by seed powder of prosopis juliflora DC. *J Hazard Mater* 2009; 169: 991-997.