

Removal of copper (II) from aqueous solution using biopolymer-based materials

NOUREDDINE ELBOUGHDIRI¹, HANA FERKOUS^{2,3}, KARIMA ROUIBAH⁴, AMEL DELIMI^{2,3}
ABIR BOUBLIA⁵, JARI S. ALGETHAMI⁶, MOHAMMED S. ALQAHTANI⁷, KRISHNA KUMAR
YADAV^{8,9*}, BYONG-HUN JEON¹⁰, YACINEBENGUERBA¹¹

¹Chemical Engineering Department, College of Engineering, University of Ha'il, P.O. Box 2440, Ha'il, 81441, Saudi Arabia

²Laboratoire de Génie mécanique et Matériaux, Faculté de Technologie, Université de Skikda, 21000, Algeria

³Département de Technologie, Université de Skikda, 21000, Skikda, Algérie

⁴Laboratory of Materials-Elaboration- Properties-Applications (LMEPA), University of MSBY Jijel, PB98 OuledAissa, Jijel 18000, Algeria

⁵Laboratoire de Physico-Chimie des Hauts Polymères (LPCHP), Département de Génie des Procédés, Faculté de Technologie, Université Ferhat ABBAS Sétif-1, Sétif, Algeria

⁶Department of Chemistry, College of Science and Arts, Najran University, P.O. Box, 1988, Najran 11001, Saudi Arabia

⁷Radiological Sciences Department, College of Applied Medical Sciences, King Khalid University, Abha 61421, Saudi Arabia.

⁸Faculty of Science and Technology, Madhyanchal Professional University, Ratibad, Bhopal 462044, India

⁹Environmental and Atmospheric Sciences Research Group, Scientific Research Center, Al-Ayen University, Thi-Qar, Nasiriyah, 64001, Iraq

¹⁰Department of Earth Resources and Environmental Engineering, Hanyang University, Seoul 04763, Republic of Korea

*Corresponding author: envirokrishna@gmail.com (K.K.Y.)

Abstract Pollution from heavy metals is increasingly recognized as a major threat to Earth's ecosystem. Due to the potential economic and ecological consequences, there is an urgent need to develop waste management systems and strategies for disposing of copper ions (Cu^{2+}) from the industrial sector. This research looked at the efficacy of adsorbents from the waste olive residue, namely raw olive waste powder (OWP) and sodium alginate biocomposite beads (OWPSA). Several factors, such as the medium's pH and the length of time in contact, were studied for their impact. Both pseudo-first-order (PFO) and pseudo-second-order (PSO) models have been used in kinetics research. Research into thermodynamics has revealed that Cu^{2+} adsorption was spontaneous, endothermic, and resulted from physical molecule interactions

Keywords: Heavy metal; Copper (II); Raw olive powder; Sodium alginate biocomposite beads; Adsorption process

1. Introduction

Several studies have been done on the adsorptive removal of heavy metal ions from aqueous solutions since adsorption is the most applied and cost-effective technique for treating high amounts of contaminated wastewater at low concentrations, owing to its high efficiency, low operating cost, and minimal sludge volume [1]. However, adsorption efficiency primarily depends on

designing and producing effective adsorbents[2]. Activated carbons have also been widely utilized to remove heavy metals and other pollutants due to their high specific surface area and pore formation. On the other hand, it is costly and needs additives to improve its capability to remove minerals[3]. Recently, different adsorbents have been utilized for heavy metals treatment of aqueous systems via adsorption. Recently, many efforts have been made to find effective biomaterials for adsorbing and removing heavy metals, including cottonseed hulls [4], tree fern [5], sawdust [6], peat [7], and banana pith [8]. Nevertheless, there is still a requirement for these adsorbents that are economical, efficient, and easily accessible. For this purpose, eco-friendly, low-cost bio-adsorbents were used in this study to remove the copper ions (Cu^{2+}).

Although several papers in the literature deal with the experimental adsorption of heavy metals, there still is a demand for additional efforts combining both experimentally obtained measurements and theoretical simulation approaches to gain more insights into the adsorption process, especially from a molecular point of view given the abovementioned considerations[9,10]. This research focuses on the adsorption of copper ions (Cu^{2+}) from an aqueous solution using agricultural waste from raw olive waste powder (OWP) and

sodium alginate biocomposite beads (OWPSA). The Effect of the pH of the aqueous medium on the absorption efficiency of both adsorbents was studied. The adsorption results were examined for a range of physical statistics models. Besides, molecular modeling investigations were carried out to lighten the molecular level interactions between OWP, OWPSA, and Cu^{+2} ions.

2. Materials and methods

2.1. Products

All products used are analytical grade: copper chloride (II) ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), sodium hydroxide (NaOH), hydrochloric acid (HCl), sodium alginate ($\text{C}_6\text{H}_7\text{O}_6\text{Na}$), and calcium chloride (CaCl_2).

2.2. Adsorbent preparation

The adsorbent used in this study originates from a local agricultural waste recovered from the first centrifugation of olives (olive skins, leaves, and pits). The olive waste (OW) is initially air-dried, then boiled and purified of impurities using a series of lavages with hot distillation water. The powder is then recovered by centrifugation (6000 rpm), dried at 353 K, then crushed and sieved. These OWs are used as adsorbents in the form of a coarse powder (OWP) and mixed with sodium alginate (OWPSA).

2.3. Bio-composite beads

In order to use the recovered powder, it is mixed with an aqueous sodium alginate (SA) solution at a concentration of 2 % (m/v) OWP. OWPSA mixed beads are produced by dispensing a homogenous solution from a syringe into a calcium chloride CaCl_2 (4 % m/v) solution and stirring the mixture for 24 hours. The surplus CaCl_2 is eliminated by lavage with distillate water many times after the combination (beads and calcium chloride solution) has been filtered. We let the beads air dry for 48 hours at ambient temperature (303 K).

2.4. Adsorbent characterization

2.4.1. pH at the zero point of charge

The pH_{pzc} (zero charge point) is a measurement of the pH of a solution. pH_{pzc} is the pH at which the positive and negative charges on the adsorbent surface are neutralized. The pH_{pzc} value is critical in adsorption processes, particularly when electrostatic forces are involved [11]:

- Suppose the pH of the solution falls below pH_{pzc} . In that case, the functional groups on the surface of our adsorbent will be protonated by the excess protons H^+ in the solution ($\text{Ad}(\text{Ad}^+)$), and the support will become a negative adsorbent attractor.
- If the pH is greater than pH_{pzc} , the functional groups at the surface will be disrupted by the existing OH^- ions in ($\text{Ad}(\text{Ad}^-)$), and the support will be a positive adsorbent attractor.

A rapid and straightforward method for determining the pH_{pzc} entails placing 50 ml of distilled

water in closed flasks and adjusting the pH (values between 1 and 12) with NaOH or HCl solution (0.1M or 1M) is a simple technique to estimate the pH_{pzc} . After that, 50 mg of the adsorbent sample is put into each vial, and the solutions are agitated continuously for 24 hours at room temperature. After obtaining the final pH, the graph $\text{pH} = f(\text{pHi})$ is generated, with $\text{pH} = (\text{pH}_f - \text{pHi})$. The isoelectric point is found where the curve intersects with the x-axis.

2.4.2. FTIR-analysis

The primary chemical functionalities present on the surface were identified using infrared spectroscopy (IR) material analysis. KBr pellets were used in this work, conducted on a Shimadzu-type FTIR spectrometer (8400S) spanning a wavelength range of 400–4000 cm^{-1} .

2.5. Adsorption experiments

The adsorption experiment was carried out at room temperature by mixing 20 mg of the adsorbent with 20 ml of a copper (II) chloride (CuCl_2) solution containing 50 mg/L. It was performed three times with stirring at 200 rpm. After each test, the sample was centrifuged for 30 minutes (6000 rpm). The residual concentrations of Cu^{2+} were evaluated by atomic absorption spectrometry (AAS) connected with a flame-type acetylene/air. The lamp was powered at 4.0 mA for copper, the slit width was 0.5 nm, and the absorbance measurement was done at 249.22 nm. The following formula is used to compute the quantity of copper adsorbed:

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

where q_e (mg/g), C_0 (mg/L), C_e (mg/L), V (L), m (g), are the uptake capacity, initial concentration, equilibrium concentration, volume of the solution, and mass of adsorbent.

3. Results and discussion

3.1. The pH of zero-charge points

The nature of the surface of the adsorbents in a known pH solution can be classified as acid, neutral, or alkaline, depending on the pH_{pzc} value, according to **Error! Reference source not found.** The pH_{pzc} of the OWP was equal to 7.5, indicating that the OWP surface is neutral or slightly alkaline. After the encapsulation, the surface of the OWPSA becomes somewhat acidic with a pH_{pzc} value of 6.05.

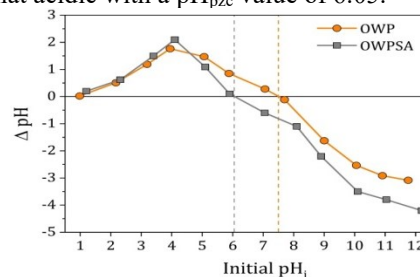


Figure.1. The isoelectric point of OWP and OWPSA adsorbents.

3.2. FT-IR analysis

The infrared spectra (FTIR) enable the identification of functional groups on the surface of an adsorbent. Often, adsorbent-adsorbate bonds are formed by these groups [11]. The FTIR of the two adsorbents (OWP and OWPSA) are shown in **Error! Reference source not found.** The FTIR spectra show the presence of absorption bands typical of lignocellulosic materials. A wide absorption band located at 3406cm^{-1} for OWP and 3421cm^{-1} for OWPSA corresponds to the vibrations of elongation of the hydrogen bonds of the hydroxyl group OH present in certain groups such as carboxylic, phenols and alcohols, and water adsorbed. It corresponds to O-H bond elongation in cellulose, pectin, and lignin.

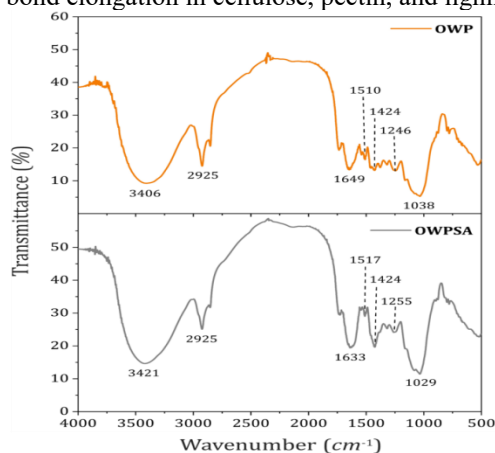


Figure.2. OWP and OWPSA FTIR spectra.

The spectra also show an adsorption band around 2925cm^{-1} for the two adsorbents resulting mainly from the stretched peak that belong to C-H of methyl and methylene structures. Additional bands are visible for the OWP at 1649cm^{-1} and between $1517\text{-}1424\text{cm}^{-1}$, and these bands correlate, respectively, to the following: bands are seen for the OWP at 1649cm^{-1} and between $1517\text{-}1424\text{cm}^{-1}$ which correspond, respectively, to the peaks of C = C of the olefinic and aromatic structures, existing in the structure of the lignin. The same vibrations are noted for the OWPSA at 1633cm^{-1} and between $1510\text{-}1424\text{cm}^{-1}$. The band identified at 1246cm^{-1} for OWP and 1255cm^{-1} for OWPSA can be attributed to ethers, esters, or phenol groups while the band located around 1038cm^{-1} and 1029cm^{-1} for OWP and OWPSA, respectively, are assigned to the vibrations of R-OH bonds of alcohol groups [11].

3.3. Parametric Study

3.3.1. Effect of contact time

Any rational installation sizing must take into account the kinetics of the adsorption process. The rate at which adsorption equilibrium is reached can vary remarkably depending on the system studied or the operating conditions. **Error! Reference source not found.** depicts the time-dependent variations in the relative amounts of Cu^{2+} ions adsorbed by OWP and OWPSA. **Error! Reference source not found.** shows that the quantity of adsorbed Cu^{2+} on OWP is increasing with time up to 360 min, with an capacity of

39.77mg/g and an efficiency of 79.54% . While in the case of OWPSA, the adsorption of Cu^{2+} is extremely quick from the first minutes indicating a great affinity between the Cu^{2+} and the OWPSA support. However, equilibrium is reached at a much greater contact time (10 hours) with a maximum adsorbed quantity of 47.27mg/g corresponding to a rating removal of 94.54% .

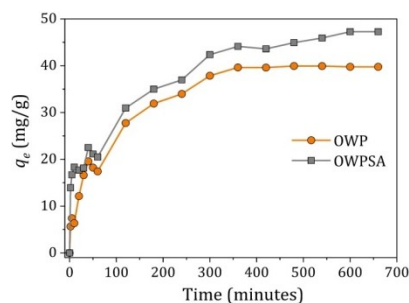


Figure.3. Effect of contact time (Conditions: $C_0 = 50\text{mg/L}$, $V=20\text{ml}$, $m=20\text{mg}$, $T=303\text{K}$).

3.3.2. Effect of pH

The variation in the quantity of Cu^{2+} ions adsorbed by OWP and OWPSA as a function of pH is shown in **Error! Reference source not found.** The data analysis reveals that the amount of adsorption Cu^{2+} on OWP and OWPSA is minimal at pH values near 3 and rapidly increases as pH increases. When the pH passes 5, the quantity of Cu^{2+} removed from the solution increases, reaches a plateau at pH 8, and achieves a maximum of 47.9mg/g (95.8%) for OWP and 49.27mg/g (98.54%) for OWPSA. At low pH, the amount of protonation of the adsorbent surfaces decreases Cu^{2+} adsorption. As the pH increases, the H^+ proton is lower, and the surface becomes negatively charged for pH values greater than pH_{PZC} of the adsorbents (6.05 for OWP and 7.5 for OWPSA) hence generating electrostatic attraction force between the adsorbents and the Cu^{2+} .

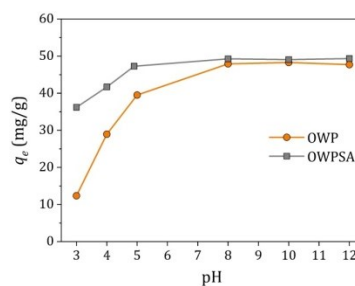


Figure.4. Effect of pH (Conditions: $C_0 = 50\text{mg/L}$, $V=20\text{ml}$, $m=20\text{mg}$, $T=303\text{K}$).

3.3.3. Effect of adding alginate

Error! Reference source not found. shows Cu^{2+} adsorption isotherms onto OWPSA and alginate. As can be seen, the two materials reveal an isotherm of Langmuir's L group. The adsorbed amount increases until it reaches a plateau indicating saturation of all sites of the adsorbent surface, demonstrating that the Cu^{2+} adsorbs homogeneously through ionic interactions guaranteed by the adsorbent surface.

a) b)

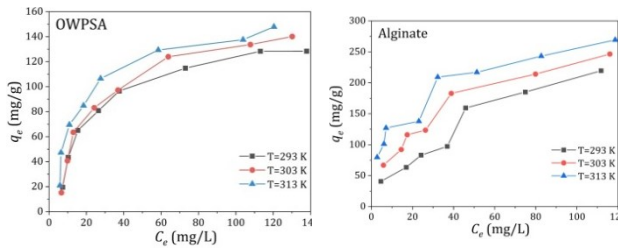


Figure.5. Copper adsorption Isotherm a) OWPSA, b) Alginate.

3.4. Adsorption kinetic models

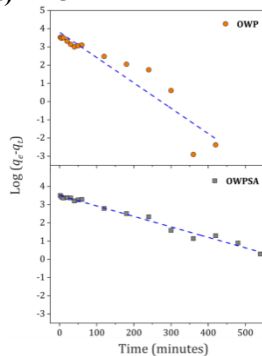
Two kinetic models, including the 1) pseudo-first-order (PFO) and 2) pseudo-second-order (PSO) models were investigated.:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

Where q_e (mg/g) is the equilibrium adsorption capacity, q_t (mg/g) is the instantaneous adsorption capacity and k_1 and k_2 are the kinetic rates, respectively. The models of PFO and PSO of Cu^{2+} adsorption kinetics on OWP and OWPSA are represented in **Error! Reference source not found...** The best model for the adsorption kinetics study is chosen according to the coefficient of determination (R^2). The PSO model best describes the adsorption of Cu^{2+} on OWP and OWPSA. The estimated adsorption capacities are highly close to the experimentally determined values.

a) PFO



b) PSO

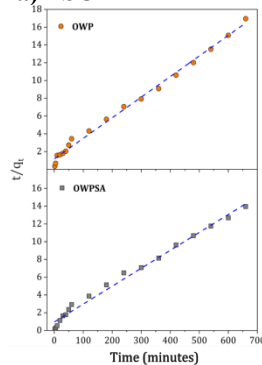


Figure.6. The Cu^{2+} adsorption kinetics on OWP and OWPSA, a) PFO model and b) PSO model.

4. Conclusion

This study aimed to evaluate the feasibility of adsorbing Cu^{2+} onto efficient adsorbents. We may draw the following significant inferences from the findings above:

- The removal efficiency of Cu^{2+} was around 79.54 and 94.54% for the OWP and OWPSA, respectively.
- The kinetics study was better simulated using the PSO model as it found a good agreement with the dynamic behavior of copper adsorption onto OWP and OWPSA.

- The adsorption processes were studied using progressive statistical physics isotherms. The SLMRG was a good fit for the adsorption equilibrium.
- The thermodynamic parameters confirmed that the processes are spontaneous, endothermic, and ruled by physical interaction.

References

1. Mack, C.; Wilhelmi, B.; Duncan, J.R.; Burgess, J.E. Biosorption of Precious Metals. *Biotechnol. Adv.* **2007**, *25*, 264–271.
2. Pap, S.; Kirk, C.; Bremner, B.; Turk Sekulic, M.; Shearer, L.; Gibb, S.W.; Taggart, M.A. Low-Cost Chitosan-Calcite Adsorbent Development for Potential Phosphate Removal and Recovery from Wastewater Effluent. *Water Res.* **2020**, *173*, 115573, Eq. (2)
3. Lee, S.-Y.; Choi, H.-J. Persimmon Leaf Bio-Waste for Adsorptive Removal of Heavy Metals from Aqueous Solution. *J. Environ. Manage.* **2018**, *209*, 382–392, Eq. (3)
4. Khan, N.A.; Ibrahim, S.; Subramaniam, P. Elimination of Heavy Metals from Wastewater Using Agricultural Wastes as Adsorbents. *Malaysian J. Sci.* **2004**, *23*, 43–51
5. Ho, Y.-S.; Chiang, T.-H.; Hsueh, Y.-M. Removal of Basic Dye from Aqueous Solution Using Tree Fern as a Biosorbent. *Process Biochem.* **2005**, *40*, 119–124
6. Bulut, Y.; Tez, Z. Removal of Heavy Metals from Aqueous Solution by Sawdust Adsorption. *J. Environ. Sci.* **2007**, *19*, 160–166, doi:10.1016/S1001-0742(07)60026-6.
7. Borgulat, J.; Mętrak, M.; Staszewski, T.; Wilkomirski, B.; Suska-Malawska, M. Heavy Metals Accumulation in Soil and Plants of Polish Peat Bogs. *Polish J. Environ. Stud.* **2018**, *27*, 537–544.
8. Yushananta, P.; Ahyanti, M. Utilization of Banana Pith Starch From Agricultural Waste As A Cationic Coagulant. *J. Aisyah J. Ilmu Kesehatan.* **2022**, *7*, 165–172
9. Boudjelida, S.; Souad, D.; Hana, F.; Benguerba, Y.; Imane, C.; Mauro, C. Physicochemical Properties and Atomic-Scale Interactions in Polyaniline (Emeraldine Base)/Starch Bio-Based Composites: Experimental and Computational Investigations. *Polymers (Basel).* **2022**, *14*
10. Behloul, H.; Ferkous, H.; Bougdah, N.; Djellali, S.; Alam, M.; Djilani, C.; Sedik, A.; Lerari, D.; Jeon, B.-H.; Benguerba, Y. New Insights on the Adsorption of Cl-Reactive Red 141 Dye Using Activated Carbon Prepared from the ZnCl_2 -Treated Waste Cotton Fibers: Statistical Physics, DFT, COSMO-RS, and AIM Studies. *J. Mol. Liq.* **2022**, *364*, 119956
11. Benamraoui, F. Elimination Des Colorants Cationiques Par Des Charbons Actifs Synthétisés A Partir Des Résidus de l'agriculture, 2014.