

The Removal Performance of Bio-Sorption on Sunflower Seed Husk for Copper and Lead Ions from Aqueous Solutions

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ABSTRACT

This study was concerned with the feasibility of using sunflower seed husk (waste material from the food industry) as a low-cost and available sorbent material to remove copper and lead ions. Sunflower seed husk was used for the biosorption of heavy metal ions (Pb(II) and Cu(II)) from aqueous solutions. The properties of natural adsorbent were characterized using Fourier transform infrared spectroscopy (FTIR). Pb(II) and Cu(II) adsorption were investigated in batch experiments through several influencing operating parameters, including contact time, sorbent dosage, initial pH, and initial concentration. The Pseudo-first-order and pseudo-second-order models were also applied to the experimental data to determine the adsorption kinetics. The results showed that adsorption of both ions fitted well by pseudo-Second-order, with determination coefficient $R^2 = 0.99$, for both ions with SSE (1.628, 1.345) for Pb(II) and Cu(II), respectively.

Keywords: heavy metal, industrial wastewater, adsorption capacity, sunflower seed husk.

INTRODUCTION

Since toxic metals have a substantial effect on ecological systems, the poisoning of the environment by these elements is a major reason for worry. Because living organisms cannot break down toxic metals, they may build up at every stage of the food chain and negatively impact every living thing. As a result, developing systems capable of removing harmful heavy metals from contaminated wastewater is of utmost significance. The removal of heavy metals from water is often accomplished by one of the following remediation techniques: precipitation and coagulation; adsorption; ion exchange remediation; or precipitation/adsorption [1, 2].

The pollution from metallic ions lasts a very long, and living creatures cannot break down the vast majority of them. Once they are prevalent in the environment, heavy metals, including mercury (Hg), cadmium (Cd), cobalt (Co), nickel (Ni), copper (Cu), arsenic (As), zinc (Zn), lead (Pb), and chromium (Cr) have the potential to cause issues in the circulatory, gastrointestinal, and neurological

systems. In addition, they cause damage to a range of organs and have been linked to an increased risk of cancer, infertility, brain damage, hearing loss, and blindness, as well as a host of other major health conditions, all of which might finally result in the death of the person who is afflicted [3, 4].

Even at extremely low amounts, the majority of the toxic metals dumped into the wastewater have been determined to be poisonous, carcinogenic, and cause substantial health issues for human beings [5]. Cadmium, copper, and lead are all elements that may often be found in aquatic ecosystems. Copper is a trace element that is necessary for all living creatures. It is responsible for catalyzing the creation of heme and the absorption of iron. An excessive amount of copper consumed may lead to several health issues, including anemia, stomach and intestinal pain, damage to the liver and kidneys, and so on [6, 7].

Copper has density, atomic weight, atomic number, and boiling point of 8960 kg m⁻³, 63.546, 29, and 2562 °C, respectively. This element can occur in oxidation states of Cu⁺³, Cu⁺², Cu⁺¹, and Cu. Copper can be utilized extensively in several

agricultural and industrial activities, specifically in manufacturing cooking utensils, coins, plumbing fixtures, pipes, electrical conductors, textiles, and antifouling paints. Also, the compounds of this element are often presented in fungicides and pesticides, wood preservatives, and copper sulfate is applied as a fertilizer [8, 9].

The oxidation states 0 and +2 are the most prevalent forms in which lead may be found. The more frequent and reactive lead form is called Pb(II), and it may produce mononuclear and polynuclear hydroxides and oxides. The production of antimonial lead (for example, lead alloys, copper alloys, and battery grids), as well as the production of semi-finished items, including blocks, bending, traps, sheet, and pipe for ammunition and caulking for both sporting and military reasons [10, 11], are the primary uses of lead. Furthermore, the manufacturing of ceramics, glass, and solder, as well as the processes involved in lithography, all need lead and its many derivatives. Lead may be found in varying quantities in some types of fertilizer. Anthropogenic sources of lead in soil and groundwater include the land use of sewage sludge, animal wastes from livestock wastewater, production, municipal refuse incineration, coal residues, and exhaust from automobiles [9, 12].

Lead (Pb) has, for an extremely extended period, been regarded as one of the heavy metals found in the environment that poses the greatest risk to human health. Ingestion of lead via the food chain may result in severe and far-reaching health problems, including cancer, bone damage, oligos, newborn hemolytic syndrome, and maybe even death [13]. Table 1 outlines the maximum contamination levels (MCLs) that should not be exceeded for any metals that may be found in potable water.

This article focuses on using activated peels of sunflower seeds husk as a natural and super-adsorbent for lead and copper (II). This can be accomplished by utilizing only activated naturally produced agricultural waste products readily

accessible, which may be an alternative to more expensive wastewater treatment processes. As a result of the strong demand for sunflower seeds, researchers suggest using this kind of agricultural waste as a cost-effective adsorbent for the removal of heavy metals.

MATERIALS AND METHODS

Contaminant

Copper and lead pollution led to the production of stock solutions of $(\text{Pb}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O})$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (made by HIMEDIA, India), both of which were held at room temperature after having a concentration of 1 kg/m^3 . Any solution may have its pollutant concentrations determined by diluting it, and the pH of the solution can be altered by adding a few drops of 0.1 M sodium hydroxide or hydrochloric acid.

Adsorbent

Natural Sunflower seed husk, the adsorbent was prepared by sinking the shells of the clam in H_3PO_4 (15%) for one hour and were kept in the oven at a temp of 100-degree centigrade until they fully dried; the seed shells were grind to a fine powder. The preparation of material involved cleans of the peels of sunflowers seeds with distilled water; the dried mixtures were ground and sieved with a size range from 355 to $710 \mu\text{m}$ to become powder, as shown in Figure 1.

Characterization techniques of adsorbent

The characteristics of the natural adsorbent were examined through Fourier transform infrared spectroscopy (FTIR), which is characterized by infrared spectrometry (FT-IR) (Shimadzu IR Affinity-1) within the range of $400\text{--}4000 \text{ cm}^{-1}$ employing tablets as KBr.

Table 1. Source, effect, and maximum permissible concentration for popular metal ions [9]

Metal	Source	Effect	MCL (kg/m^3)
Cd	Welding, nuclear fission plants, electroplating.	Reproduction problems, Renal dysfunction, Lung disease, Lung cancer, bronchitis.	0.000003
Pb	Pesticides, automobiles, coal burning.	Damage to the brain, kidney, and liver, cardiotoxic, congenital paralysis, anemia, high blood pressure, infertility, and reduced learning abilities.	0.00001
Zn	Brass manufacture metal plating.	Zinc fumes have a corrosive effect on the skin and have a negative impact on nervous membrane.	0.003
Cu	Mining, metal piping, pesticide production.	Uraemia, anemia, hypertension, sporadic fever, coma, damage to the kidney and liver.	0.002

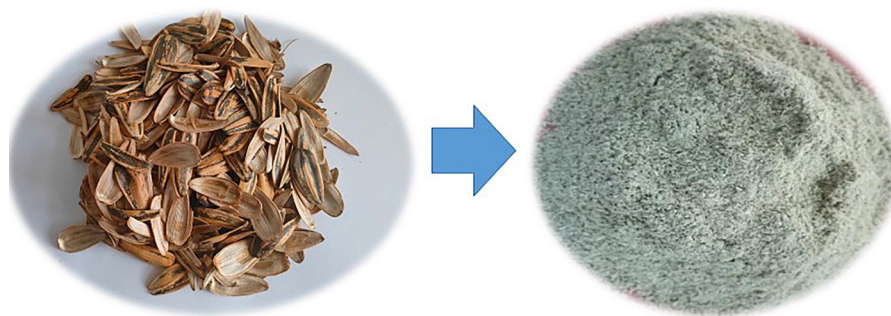


Figure 1. Sunflowers seeds husk wastes powder

Mechanisms of adsorption kinetics

Adsorption kinetic models have been employed in this study to quantify the aqueous absorption rate and the needed adsorption time [14]. These models were chosen due to their ability to explain the sorption process that occurs on the sorbents. The contaminating molecules and the adsorbent particles connect in a way that might be either physical or chemical. This results in the adsorption process. In most cases, the adsorption process and the phase of the adsorption that predominates are defined by making use of one of the following three kinetic models:

Pseudo-first order

The following formula serves as a representation of the Pseudo-First-Order model [15]:

$$qt = qe(1 - e^{-K_1t}) \quad (1)$$

where: q – the quantity of the pollutant, which was adsorbed at a specific time (t) (mg/g);
 qe – shows the amount of contaminant, which was adsorbed under equilibrium circumstances (mg/g);
 k – seems to be the pseudo-first-order adsorption rate (min^{-1}).

Pseudo-second order

It is possible to quantify the Pseudo-Second Order with the help of the following formula [16]:

$$qt = \frac{t}{\left(\frac{1}{k_2qe^2} + \frac{t}{qt}\right)} \quad (2)$$

where: k_2 – the second-order sorption constant rate in units of milligrams per milligrams per minute. Calculating the initial sorption rate at very low beginning amounts is possible using the pseudo-second-order

adsorption kinetic model, which may be applied to this problem.

Batch adsorption study

Adsorption investigations were conducted with natural compounds. Different conditions were used to study the adsorption of (copper and lead) ions. Experiments were carried out in an Orbital Shaker by stirring a known amount of natural compound in 0.001 m^3 of the synthetic solution of the pollutants Pb(II) and Cu(II) each pollutant was studied separately with 0.05 kg/m^3 initial concentration. Batch experiments were implemented with different contact times (0–12000 s), initial pH of the solution (2–7) and initial contaminant amount (0.005–0.2), and sorbent dosage ($1\text{--}20 \text{ kg/m}^3$) to determine the remaining heavy metal concentration. Whatman (No. 40) filter paper to use to separate the adsorbent from the aqueous solution. Then the filtered solution was analyzed using Atomic absorption spectrophotometer (AAS) (Sens AA, Japan) to measure the concentrations of copper and lead ions. The amount of heavy metal adsorbed onto the natural compound, qe , has been determined utilizing Eq (1) [17, 18].

$$qe = (C^{\circ} - Ce) V / m \quad (3)$$

where: qe (mg/g) – the quantity of ions adsorbed per unit mass of adsorbent;
 C° and Ce (ppm) – the initial and equilibrium heavy metal amounts, respectively,
 V (L) – the ions solution volume;
 m (g) – the adsorbent mass.
 Eq. 4 was used to compute heavy metal removal efficiency ($R\%$) from the natural adsorbent.

$$R = \frac{(C^{\circ} - Ce)}{C^{\circ}} \times 100\% \quad (4)$$

RESULTS AND DISCUSSION

Characteristics of the biosorbent

Infrared measurements (FTIR) of sunflower hulls (Fig. 2) revealed the presence of such functional groups as –OH and –NH (3294 cm^{-1}), amide groups (1632 cm^{-1}), and –CH₂ (2357 cm^{-1}), and –P=O (1041 cm^{-1}) groups.

Effects of contact time

When attempting to define the diffusion of pollutants between solid and aqueous phases, one of the most important factors to consider is the amount of time needed to attain equilibrium in batch research. As a result, the impacts of contacting time on the adsorption of copper (II) and lead (II) onto the novel adsorbent were examined at a variety of contact periods (0 to 12000 s). Experiments were carried out many times with varying starting amounts of lead (II) and copper (II), ranging from 0.005 to 0.2 kg/m³.

The original pH range was from 2 to 7, and the varied doses of natural adsorbent ranged from 1 to 20 kg/m³, which was done so that the impacts of the heavy metal amount could be understood on the natural adsorbent performance. It can be observed from this figure that the contaminant removal percentages climbed rapidly during the first hour of these studies but subsequently slowed down significantly throughout the remaining hours of these investigations. The findings of these experiments are shown in Figure 3. An increase in occupied locations on the surface of the adsorbent is to blame for the slower adsorption rate. 10800 s and 7200 s are necessary to attain the maximal adsorption of lead (II) and copper(II), respectively, to 71 and 69%.

Sorbent dosage

The impacts of the amount of adsorbent on the removal of Cu(II) and Pb(II) were explored utilizing masses of the newly modified adsorbent (between 0.05 and 2 g/100 mL), which was done

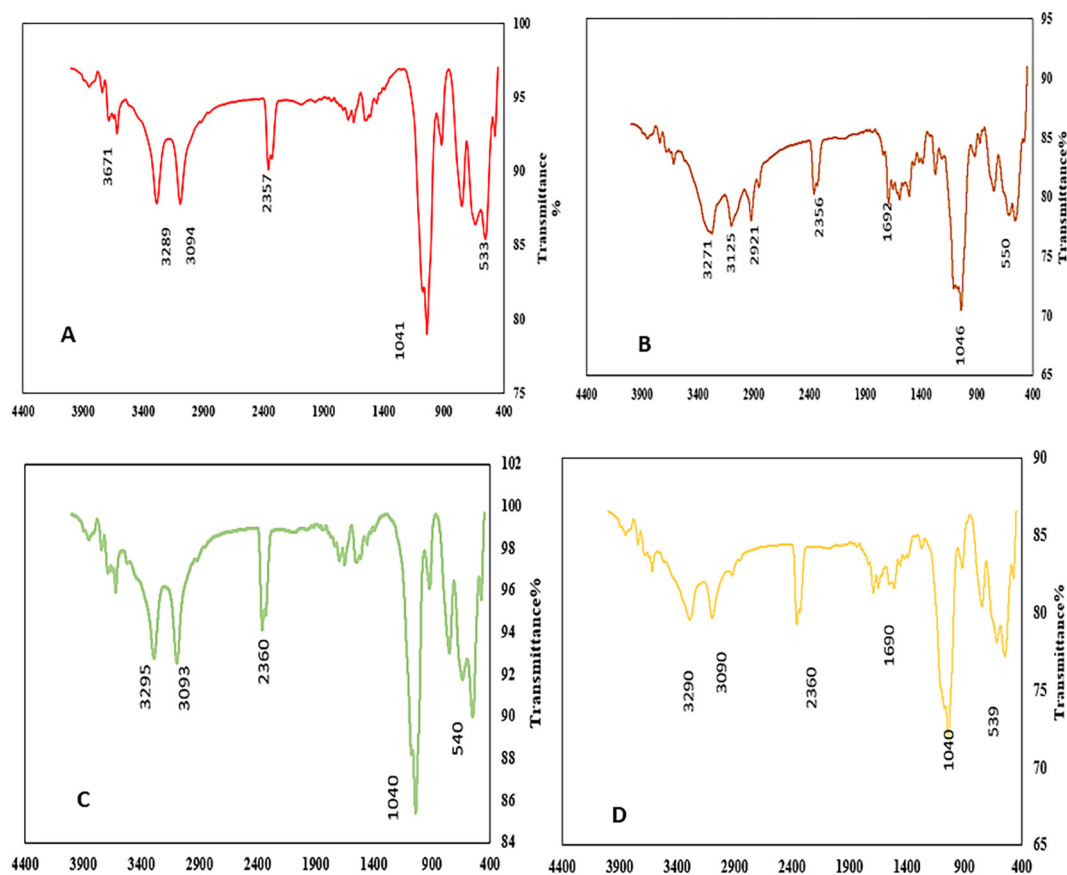


Figure 2. FTIR of (a) sunflower hulls, (b) modified sunflower hulls, (c) sunflower hulls after interaction with Cu(II), and (d) after interaction with Pb(II)

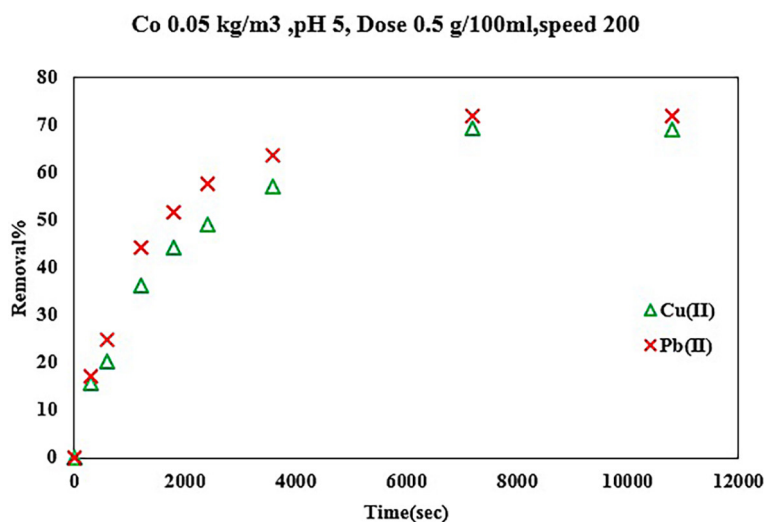


Figure 3. Effect of time on adsorption capacity

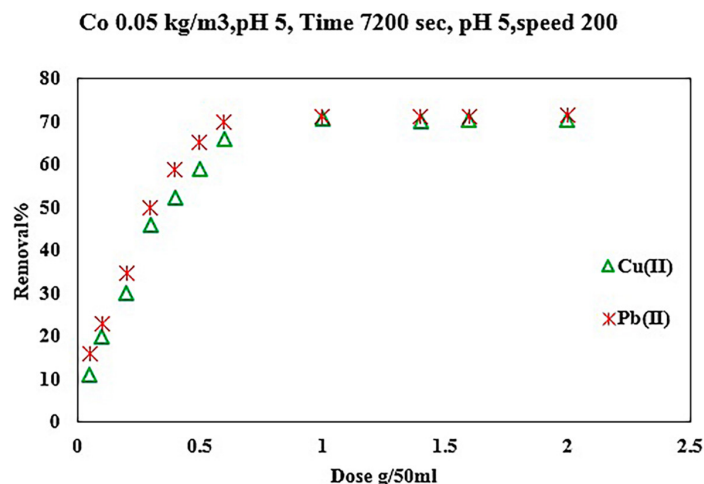


Figure 4. Effect of adsorbent dose on removal percentage

while maintaining the magnitudes of cobalt, agitation speed, contact time, and initial pH at 200 rpm, 200 minutes, and 0.050 kg/m³, 5, respectively. Figure 4 demonstrates that increasing the dosage of the proposed adsorbent from 0.5 to 8 kg/m³ results in a considerable rise in the amount of Cu(II) and Pb(II) that is removed, with the former going from 11 to 69% and the latter going from 16 to 70%, respectively. Nevertheless, increasing the dosage to more than 0.8 grams per one hundred milliliters did not improve the elimination efficacy [19].

Initial values of pH and initial concentration

Within the range of 0.005 to 0.2 kg/m³, the influence of the initial amount on the sorption effectiveness of copper and lead ions was examined. The range was used since these ions were

being sorbed. Because of an increase in starting amount within the specified range, the removal efficiency of the metallic ions onto the produced sorbent at pH equal to 7 reduced from higher magnitudes (more than 77%) to lower magnitudes (higher than 30%), as shown by Figs. 5 and 6. The major explanation for this behavior may be that there are adequate sites for sorbing substantially more metallic ions from an aqueous solution. The sorption of metals steadily increased throughout the process of increasing the original pH; a change in pH from 2 to 7 might induce a noteworthy rise in the elimination of adopted metallic ions within the range of (30–72%) for an initial amount of 0.005 kg/m³. The key to explaining the pH dependency data for copper and lead ions might be found in the surface characteristics of the adsorbent as well as the type of metal ions that are available in the aqueous solution [20]. It

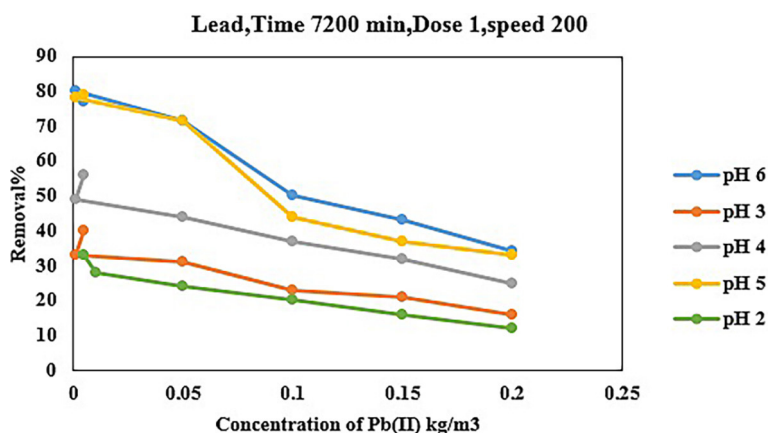


Figure 5. Effect of initial values of pH and concentration on the removal of copper ion from aqueous solutions by natural adsorbent

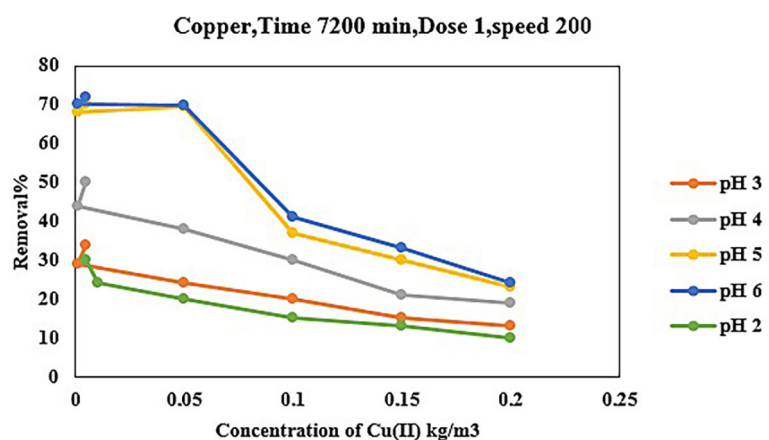


Figure 6. Effect of initial values of pH and concentration on the removal of Lead ion from aqueous solutions by natural adsorbent

was discovered that raising the amount of Pb(II) and Cu(II) from 0.005 to 0.2 kg/m³ resulted in a reduction in removal efficacy of 73 percent and 77 percent, respectively, down to 16 and 20 percent. This reduction in removal effectiveness might be explained by the restricted number of vacant sites on the adsorbent surface, which occurs in conjunction with a rise in heavy metals [21, 22].

Kinetic of adsorption

Kinetic experiments of the difference of Pb(II) and Cu(II) adsorption with contact duration onto the natural adsorbent at different initial amounts of Pb(II) and Cu(II) have been fitted with non-linear analysis utilizing the “Solver” software in Microsoft Excel 365. This research was conducted on the normal adsorbent at different initial amounts of Pb(II) and Cu(II). The best circumstances for carrying out the kinetic trials have been those that had been determined from

the batch experiments that came before them. The parameters of the kinetic models are shown in Table 2 depending on formulas (1) and (2) that were determined from the processes of fitting the data. As can be seen in Figure 7a and Figure 7b, statistical metrics such as the sum of squared error (SSE) and the determination coefficient (R²) are calculated to describe the convergence between the experimental data and theoretical models. The

Table 2. The parameters of the kinetic models

Order	Parameters	Cu(II)	Pb(II)
Pseudo-first order	q_{max}	7	7.2
	K1	0.045	0.032
	SSE	2.329	1.852
	R2	0.99	0.99
Pseudo-second order	q_{max}	6.99	7.541
	K1	0.009	0.008
	SSE	1.628	1.345
	R2	0.99	0.99

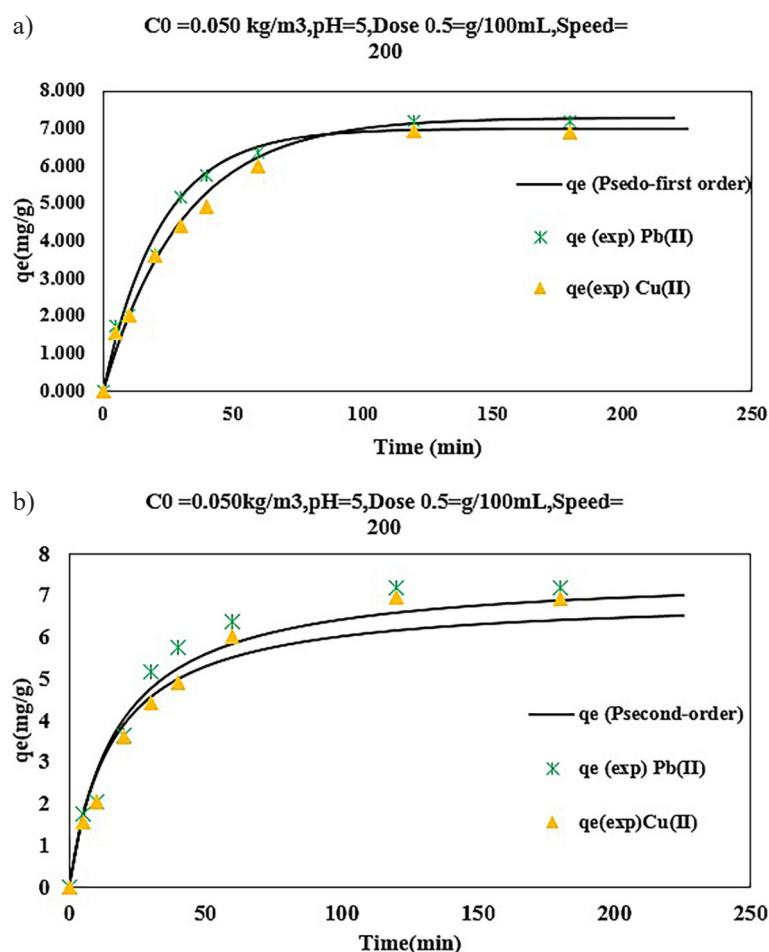


Figure 7. Kinetic models for sorption of copper and Lead ions in comparison with experimental measurements

Pseudo 2nd model is the most accurate in explaining the adsorption process of Pb(II) and Cu(II) after kinetic fitting was performed on the data shown in this figure and table. This model has the highest R² value and the lowest SSE value. Additionally, the model's applicability was shown by the observed amount of contaminant that was adsorbed (q_e) was very near to the anticipated magnitudes. These findings provided further evidence that the elimination of Pb(II) and Cu(II) is due to the formation of chemical bonds (for example, chemisorption) [23].

CONCLUSION

In order to achieve its goal of eliminating Pb(II) and Cu(II) ions from aqueous solutions, the research project used sunflower seed husk husks, a waste material produced by the food industry. The findings demonstrated an adequate level of elimination; This sorbent effectively removes Pb(II) and Cu(II) from aqueous solutions, as shown by its

ability to do so with high removal rates. Pseudo-second-order and pseudo-first-order models depend on the sequence of chemical reactions precisely represent experimental points, which confirms the chemisorptive character of the process.

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