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Using Eucalyptus Peels as a Permeable Reactive Barrier for Treating Groundwater Contaminated with Copper Ions – A Simulation with COMSOL Software

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ABSTRACT

This study investigated the use of eucalyptus peels as a permeable reactive barrier (PRB) for treating groundwater contaminated with copper ions. Activated carbon was produced from eucalyptus peels, and its adsorption capacity for copper removal was evaluated through laboratory experiments. COMSOL software was used to simulate the performance of the eucalyptus peel-based PRB in order to optimize the design as well as predict the efficiency and longevity of the barrier. Batch studies were conducted to evaluate how factors such as the initial concentration of the contaminant, pH level, contact time, amount of sorbent used, and agitation speed affected the results. The results show that the optimal values of these factors were a 50 ppm concentration, a pH of 6, an 80-minute contact time, a dosage of 2 mg per 100 ml, and a stirring speed of 250 rpm. These findings demonstrate that eucalyptus peels, being an agricultural waste product, can be effectively converted into activated carbon with a high adsorption capacity (equal to 91.5%) for copper ions. To analyze the data, researchers utilized COMSOL Multiphysics 3.5a software, which employs the finite element method to solve the equations that describe the one-dimensional (1D) movement of copper under equilibrium conditions. Compared to other organic and inorganic adsorbents commonly used in PRBs, eucalyptus peels showed promising results in terms of adsorption capacity and cost-effectiveness. This study contributes to the development of innovative and sustainable remediation strategies for groundwater contaminated with heavy metals like copper. The findings demonstrate the potential of eucalyptus peels as a viable alternative to traditional adsorbents used in PRBs, promoting the use of renewable materials in environmental management and indicating that the PRB significantly impedes the movement of the copper plume. Ultimately, the predictions from the COMSOL simulations were very close to the actual experimental results, with a root mean square error (RMSE) of less than 1%.

Keywords: permeable reactive barrier, copper, eucalyptus peels, activated carbon, ground water, migration.

INTRODUCTION

One of the most pressing issues facing the ecosystems today is the widespread pollution of ground water and surface water with heavy metals (Pandey et al., 2019). These high levels of heavy metals primarily result from human activities (Faisal et al., 2022). Copper was chosen for removal from groundwater due to its toxicity, prevalence in contaminated water sources, as well as the economic and regulatory pressures that make addressing these issues a priority (Di Natal et al., 2008). The water from agricultural areas and surface runoff seeps into the ground water, potentially leading to significant contamination (Saeed et al., 2024). For many years, traditional and often costly remediation methods like "impermeable barriers" and "pump and treat" systems have been employed. However, the high expenses and operational challenges associated with these passive in situ techniques make them less favorable. These barriers are designed to capture the pollutants that move through the saturated zone, thereby promoting the natural processes that help clean the soil (Faisal et al., 2021). The movement of heavy metals dissolved in groundwater can be managed through the reactions that cause these metals to precipitate or be absorbed, as well as through the chemical interactions that bind metals to reactive materials found in (PRB) (Mayacela-Rojas et al, 2021; Li and Liu, 2022). The technology behind PRB, which utilizes affordable and widely available materials, requires a comprehensive evaluation of the environmental impacts associated with the production of reactive materials. Consequently, it is essential to advance the creation of reactive materials or absorbent that are not only more effective and cost-efficient but also safe for the environment (Budania and Dangayach, 2023). One of the critical steps in designing a PRB is selecting the right filler for the barrier. Consequently, numerous research centers are on the lookout for new adsorbent to enhance decontamination efficiency (Roehl et al., 2005). Activated carbon serves as a reactive media (sorbent) in PRBs due to its ability to effectively remove a wide range of inorganic and organic contaminants from various environments; however, it remains quite costly. This has led many researchers to focus on developing low-cost sorbents (Babel and Kurniawan, 2003). As a result, various effective alternative materials have been explored as reactive agents in PRBs. Some studies have utilized waste as budget-friendly materials (Raheem et al., 2022), while others have successfully created effective carbon from inexpensive sources (Yin et al., 2017). While various organic materials have been explored for their potential as adsorbents in PRBs, there is limited research specifically focusing on eucalyptus peels. This study aimed to establish their effectiveness in removing copper ions from contaminated groundwater, thereby expanding the range of sustainable materials available for environmental remediation. The effectiveness of using agricultural waste, such as eucalyptus peels, in PRBs has not been thoroughly investigated. This study aimed to provide empirical data on the adsorption capacity and efficiency of eucalyptus peels, contributing to a better understanding of how organic waste can be utilized in water treatment applications. The application of COMSOL software for simulating the behavior of eucalyptus peels in PRBs represents a novel approach in this context. The study sought to develop a computational model that can predict the performance of the barrier, which is essential for optimizing design and implementation strategies in real-world scenarios.

The use of eucalyptus peels in PRBs represents a promising method for treating copper-contaminated groundwater, combining sustainability with effective contaminant removal strategies. The integration of simulation tools like COMSOL enhances the understanding and application of this technology in environmental management. The sufficient number of peels used in producing activated carbon for PRBs is justified by the need for effective adsorption capacity, cost-effectiveness, sustainability, and the potential for performance optimization. In a study by Hmood (2013), the effectiveness of zeolite as a reactive material in the PRB technique for eliminating cadmium from polluted aquifers was examined. The research found that high removal rates were achieved under specific batch experimental conditions, with pH levels varying from 2 to 8. Additionally, the Langmuir sorption model was shown to accurately describe how cadmium ions are absorbed by zeolite. In a study by Ali et al. (2019), researchers investigated the potential of using olive seeds as a PRB to effectively remove copper ions from polluted groundwater. They looked into several factors, for example the Cu^{2+} initial concentration, pH levels, agitation speed, contact time, and the amount of sorbent used. Under the best conditions, they achieved an impressive 99% removal rate of copper. Additionally, the study noted that olive seeds showed minimal copper dissolution, as demonstrated by leaching tests. Both numerical modeling and experimental findings supported the effectiveness of olive seeds in reducing the copper pollution in groundwater.

The authors hypothesized that activated carbon produced from eucalyptus peels will demonstrate a significant adsorption capacity for copper ions, comparable to or exceeding that of other commonly used materials in PRBs. The authors expect that the COMSOL simulations will accurately reflect the interactions between copper ions and the eucalyptus peel-based PRB, allowing for predictions about the performance of the barrier over time. The study anticipated that utilizing eucalyptus peels not only provides an effective means of treating copper-contaminated water but also offers a sustainable and cost-effective alternative to traditional materials, thus promoting environmentally friendly practices in groundwater remediation.

The purpose of the current study was to create a new adsorbent that can be used in PRB technology to effectively remove Cu ($^{2+}$) ions from contaminated groundwater. The project followed several key steps: (1) developing a sustainable method to produce powdered activated carbon from eucalyptus leaf, which supports an eco-friendly approach and reduces waste, (2) testing how well this adsorbent works at removing copper from water solutions, and (3) evaluating the one-dimensional transport of copper through the reactive material (eucalyptus peels) using both numerical modeling with COMSOL Multiphysics 3.5 software and fixed-bed column experiments. This software provides a robust interactive platform for solving and modeling engineering and scientific challenges involving partial differential equations (PDE) (Cabrera et al 2024). Therefore, this study is significant, as it explores the potential of using eucalyptus peels (EP) as an effective adsorbent and low-cost in PRBs for treating groundwater contaminated with copper ions (Cu^{2+}).

METHODOLOGY

Material

Eucalyptus peels were cut into small pieces and dried in an electric oven at 105 degrees Celsius for two hours before being ground down. After being washed with hot water, the peels were dried again in the same electric oven. Once fully dried, they were blended into a fine powder and sifted to separate the particles into sizes between 75 μm and 600 μm, with the goal of isolating the smallest molecules (Fig. 1). In the 1st step, dried eucalyptus peels are placed in glass containers. After that a 3 M solution of phosphoric acid is carefully added to the container with the eucalyptus peels, using a soaking ratio of 2 grams of peels to 4 milliliters of the acid, at 25 °C for 24 hrs. After soaking, the peels were left to air dry partially before being placed in an oven at 120 °C for two hours to complete the drying process.

In the 2nd stage, the eucalyptus peels were placed in a metal bowl and heated to 500 °C for 1 hr. This heating duration was selected based on earlier experiments with various heating times. After 1 hr, the peels were then washed with this hot water until the pH level reached 7. Next, the material was dried to eliminate any unwanted moisture. Finally, the dried peels were crushed and sieved to obtain powdered activated carbon from agricultural solid wastes, which were used in the current groundwater treatment experiments in this study (see Figure 1).

Figure 1. Powdered activated carbon from eucalyptus peels (EP)

Batch experiments

The experimental batch was designed to control certain factors while varying others. The temperature was maintained at 25 degrees Celsius to conduct sorption isotherm experiments. The interaction durations were set at 20, 40, 60, 80, 100, and 120 minutes. The pH levels of 2, 4, 6, and 8 were explored. Different sorbent dosages were tested, ranging from 0.1 to 5 grams of activated carbon per 100 milliliters. Additionally, copper concentrations of 250, 200, 150, 100, and 50 mg/l were examined, along with agitation speeds of 250, 200, 150, 100, and 50 revolutions per minute (rpm).

The experiment utilized a set of 250 ml conical flasks, each filled with 100 ml of a Cu ($^{2+}$) solution that started at a concentration (= 50 mg/l). To each flask, 2 grams of a powdered activated carbon from eucalyptus peels (EP) were added. The flasks were kept in motion on a high-speed orbital shaker, operating at 250 rpm. From each flask, a consistent volume of 20 ml was extracted and passed through Teknik No.1 filter paper to remove the adsorbent. After filtering, 10 ml of the clear solution was collected for analysis to determine the concentration of any remaining contaminants. This concentration was measured using an atomic absorption spectrophotometer (AAS). The contaminant amount that adhered to the adsorbent was calculated using a mass balance method. On the basis of the most effective experimental outcomes, the researchers calculated the amount of copper retained in the powdered activated carbon made from eucalyptus peels (EP) using:

$$C_s = (C_o - C_e)\frac{V}{m} \quad (1)$$

where: C_o and C_e is initial and equilibrium Cu concentration in solution (mg/L), V is the solution volume in the flask (L), and m is the mass of the powdered activated carbon made from eucalyptus peels (EP) in (g).

Continuous experiments

The setup of the adsorber utilized consists of a Perspex column that stands 80 cm tall and has a diameter of 5 cm. It includes seven testing ports positioned at various heights: 70 cm, 60 cm, 48 cm, 42 cm, 36 cm, 24 cm, and 12 cm from the top. To create these ports, stainless steel fittings with Viton stoppers are necessary. The column is filled with a soil sample that reaches a depth of 36 cm from the bottom. Above this soil layer, there is a 6 cm deep layer of activated carbon. Furthermore, there is an additional layer of soil that is 18 cm deep above the activated carbon. For the column tests, two flow rates have been chosen: 5 and 10 ml/min. Over a span of 25 hours, the concentration of copper in the effluent from the testing ports was tracked. Water samples were collected at regular intervals of 5, 10, 15, 20, and 25 hours from these ports, placed directly into glass vials, and subsequently analyzed using an atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

The influence of batch tests

Contact time

To effectively remove contaminants, the contact time in experiments must be set to a specific duration that allows the system to reach equilibrium concentrations. As shown in Figure 2, the impact of contact time on the removal of Cu^{+2} ions at a temperature of 25 °C indicates that the absorption of contaminants is much faster during the initial phase of the sorption process compared to later stages. This results in a noticeable quick increase in the percentage of removal. In general, longer contact times correlate with higher removal percentages, as noted by researchers (Ali et al., 2019; Rikabi et al., 2024). The data shows that 91.5% of Cu^{2+} was removed from the EP within 80 minutes, and subsequent experiments were conducted using this same contact duration.

Initial pH of the solution

This is one of the most critical parameters in batch experiments, greatly affecting the processes for remediating heavy metals. The sorption of copper ions onto EP was studied using various pH levels ranging from 2 to 8, with an initial contaminant concentration (50 mg/l) and various contact times at 25 °C. Figure 3 reveals that the highest sorption of copper ions onto EP occurred at a pH of approximately 6, achieving maximum removal efficiencies of 91.5% for copper on EP (Saeed et al., 2024).

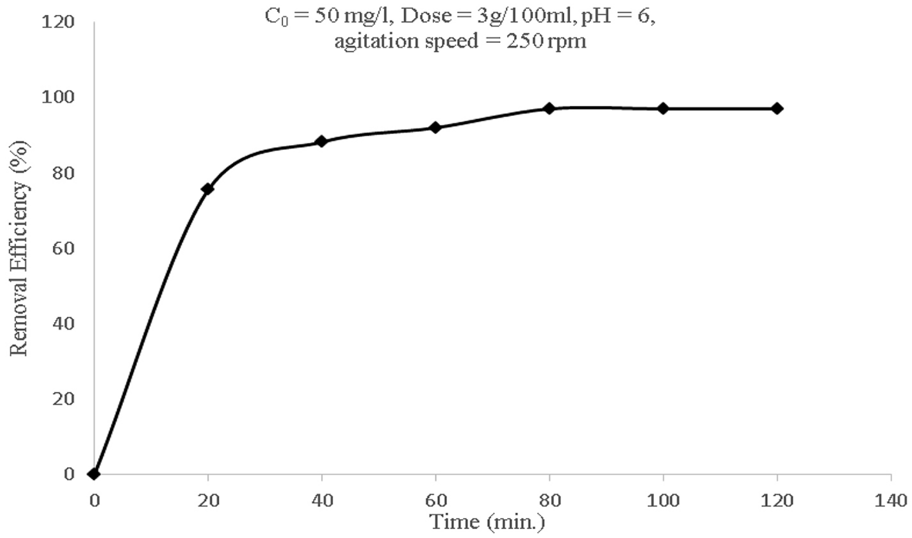

Figure 2. Removal (%) of Cu^{+2} onto EP with contact time

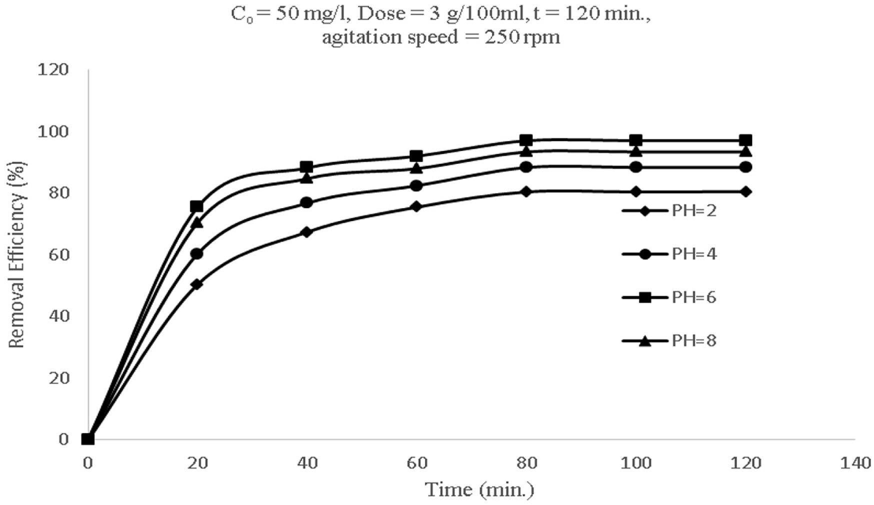

Figure 3. Removal (%) of Cu^{2+} with pH solution

The influence of activated carbon dosage

The study investigated how the mass of a sorbent affects the efficiency of copper removal from a solution, using a specific setup with a pH of 6, an initial copper concentration of 50 mg/l, and a stirring speed of 250 rpm. The researchers tested various sorbent masses ranging from 0.1 to 5 grams per 100 ml of water. As shown in Figure 4, an increase in sorbent mass led to higher removal efficiency. This is because larger amounts of sorbent offer more active sites for copper ions to attach compared to smaller amounts (Rahmani et al., 2010).

Initial concentration of copper

Different initial concentrations of copper were prepared to analyze how they relate to removal efficiency. Figure 5 illustrates that the removal efficiency decreases as the initial concentration of copper increases. Specifically, the efficiency of removing Cu^{2+} dropped from 92% to 60% when the initial concentration rose from 50 mg/l to 250 mg/l. This decline can be attributed to the fact that higher concentrations create a stronger driving force for copper ions to move from the solution to the sorbent surface, which limits the availability of sorption sites, especially in the early stages of the process (Abdulhasan et al., 2023; Ibrahim et al., 2024).

Agitation speed

Researchers conducted experiments using various agitation speeds to investigate how these speeds affect the efficiency of copper ion removal, while keeping other factors constant, such as a pH of 6, an initial contaminant concentration of 50 mg/l, and a contact time of 80 minutes

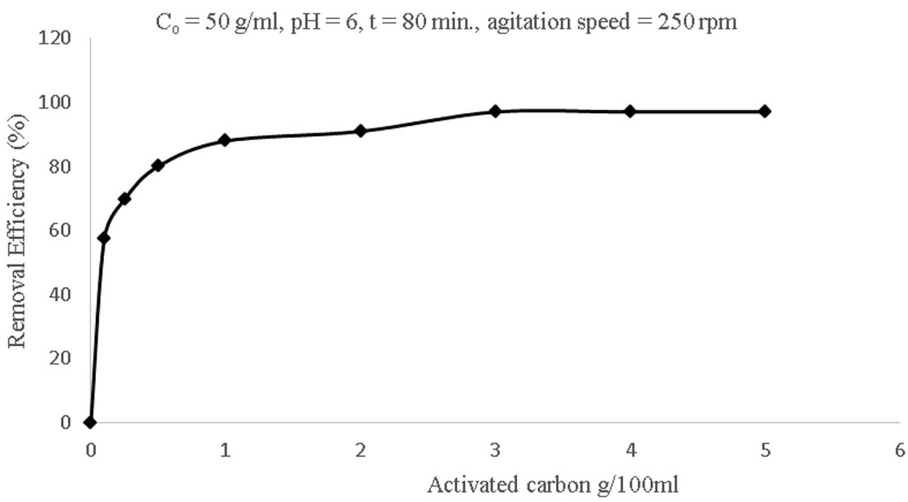

Figure 4. Removal (%) of Cu^{+2} with EP dosage

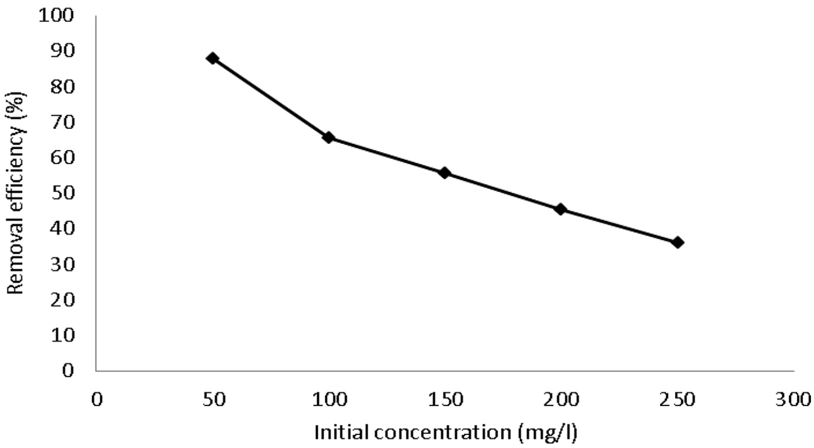

Figure 5. Removal (%) of Cu^{2+} with pH solution on initial concentration

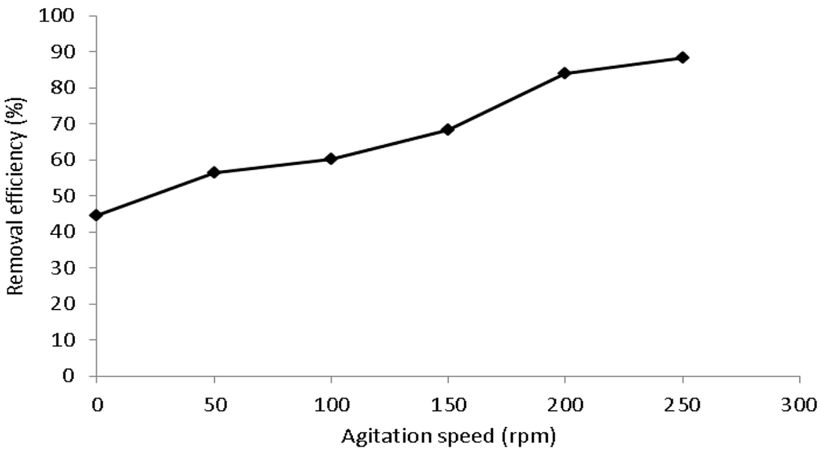

Figure 6. Removal (%) of Cu^{2+} with pH solution on agitation speed

Figure 6 illustrates that increasing the shaking speed from 0 to 250 revolutions per minute (rpm) significantly boosted the removal efficiency from 74.1% to 91.5%. This improvement in efficiency is due to the fact that higher agitation speeds facilitate the movement of heavy metal ions toward the sorption sites on the sorbents. Essentially, as the agitation speed increases, the Nernst film which creates resistance to the movement of contaminants toward the solid phase becomes thinner or may even disappear entirely at higher speeds (Al-Mansoria et al., 2020).

Modeling application

Advection dispersion processes are responsible for the migration of copper in porous media, enabling to represent the one-dimensional system of copper migration with Formula 2 (Jain et al., 2015).

$$D_z \frac{\partial^2 c_{Cu}}{\partial z^2} - V_z \frac{\partial\, c_{Cu}}{\partial z} = \frac{\partial\, c_{Cu}}{\partial t} + \frac{\rho_b}{n} \frac{\partial (q)}{\partial t} \quad (2)$$

where: C_{Cu} represents the amount of copper present in water, V_z denotes the flow speed, D_z is the coefficient that measures how copper disperses along the z direction, ρb refers to the bulk density of the dry material that absorbs copper, and q indicates the quantity of copper attached to the solid surface.

The flow domain is designed as a one-dimensional laboratory-scale column. A copper solution with a concentration of 50 mg/l was introduced into the packed columns from the bottom. The essential constants and parameters for both the PRB bed and the sandy soil bed used in the one-dimensional solute transport model are detailed in Table 1. Figure 7 presents a comparison between the theoretical predictions from the COMSOL model and the experimental results for copper transport at the same

Table 1. Constants and parameters utilized in the Cu^{+2} transport in one-dimensional column model

Item	Location	Type/Value
Aquifer characteristics	Aquifer	Sandy soil bed depth before PRB(cm) = 36 Sandy soil bed depth after PRB (cm) = 32
		Longitudinal dispersivity (αL, cm) = 35.1
	PRB	Depth of barrier bed (cm) = 6
		Longitudinal dispersivity (αL, cm) = 11.6
Initial condition	C(z,0) (mg/l) = zero	
Boundary conditions	C(0,t) (mg/l) = 50	
	Advective flux ($\frac{\alpha C}{\alpha z}$) at the top of the bed = zero	

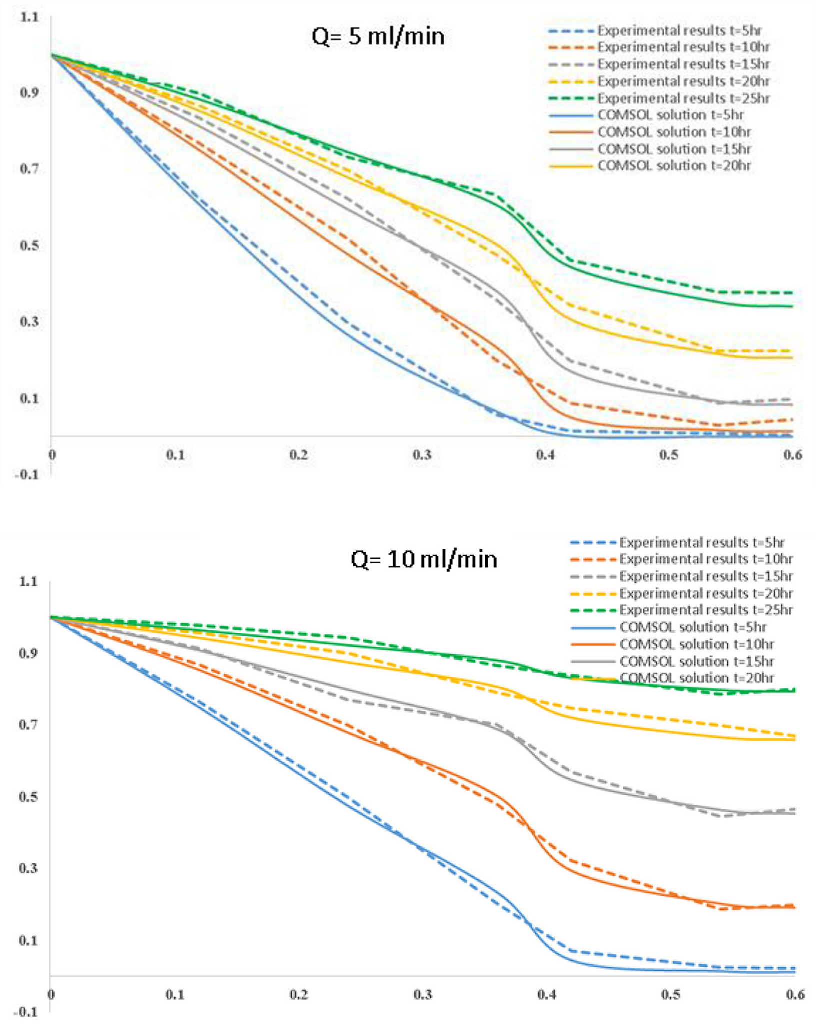

Figure 7. The compared the predicted copper amounts from the COMSOL simulations with experimental results at two different flow rates

time intervals and flow rate of 5 mL/min. The figure reveals a strong alignment between the experimental data and the expected outcomes. To measure this alignment, the root-mean squared error (RMSE) was used as a statistical tool (Krause et al., 2005). RMSE was calculated to be less than 0.1 percent, indicating a robust correlation between the results.

CONCLUSIONS

The batch experiments demonstrated that the interaction between copper and electrokinetic processes (EP) significantly influenced various factors, such as interaction time, copper concentration, pH level, agitation speed, and the amount of activated carbon used. The optimal conditions for achieving the highest removal efficiency of Cu^{2+} (91.5.5%) were found to be 80 minutes, a concentration of 50 mg/L, a pH of 6, an agitation speed of 250 rpm, and a dosage of 2 g per 100 ml.

A one-dimensional numerical model, developed using COMSOL software under equilibrium conditions, indicated that EP is an effective method for controlling the spread of copper plumes. Additionally, there was an excellent agreement between the predicted and experimental results, with a (RMSE) of less than 0.1%.

The experimental results confirmed that EP is a practical and cost-efficient reactive media suitable for utilization in PRBs to remove Cu ($^{2+}$) from contaminated groundwater.

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