Simulation Study of Copper Ions Adsorption from Wastewater by Using Raw Rice Husks

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ABSTRACT

Green bio-adsorption is a common practice in wastewater treatments. The adsorption capabilities of raw rice husks to remove copper ions from wastewater are studied. The adsorption capacity of raw rice husks can be determined empirically through experiments, but it can be time-intensive and expensive due to the inherent complexities of the adsorption process, significant labor and resources required. Simulation using the Fixed-bed Adsorption Simulation Tool, FAST is promoted as an effective prediction approach that offers a more efficient and cost-effective means of generating simulated result, providing a viable solution to the challenges associated with traditional experimental methods. This paper studies the impacts of contact time, initial ions concentration, and adsorbent dosage on the adsorption process via raw rice husks. The contact time is 30minutes, with 1- 50ppm initial copper ions concentration and 0.025-0.15grams adsorbent dosages. Simulated results display that percentage adsorption increases with contact time and reach adsorption equilibrium after 10 minutes with an optimum of 99.8% adsorption. The percentage adsorption is decreased with adsorbate concentration, where an optimum of 90% adsorption occurs at 1ppm. The adsorption capacity is increased with adsorbent dosages. The optimum adsorption percentage of 99.6%, occurs at 0.15grams. Langmuir Isotherm shows the best fit model in predicting the trendline of the breakthrough curve.

Keywords: Adsorption, wastewater treatment, raw rice husks, copper ions

INTRODUCTION

This paper is to study the efficiency of rice husks as a green natural adsorbent in removing the copper ions from the wastewater through the batch adsorption using simulation tool. The utilization of rice husks as a green adsorbent is encouraged in Malaysia due to the 12th Malaysia Plan to boost the national rice production to 75% [1]. The abundance of rice as a staple food and its widely cultivation in Malaysia can also meet the demand for using rice husk in a large scaling of adsorption process [2]. This study is in line with the idea of turning waste into wealth, and the Sustainable Development Goal (SDG) 12 and 13, where rice byproduct is feasible to be converted into valuable product such as biosorbent and reduced generation and emission of GHG to mitigate climate change.

The objective of this research is to study the impacts of parameters, including contact time, initial copper ions concentration and adsorbent dosages, on the removal of copper ions from wastewater through the simulation software, FAST. The second objective is to study the adsorption isotherms including Langmuir and Freundlich isotherm based on the comparison of correlation coefficient.

Since this current work refers to the parameters from the previous study, certain variables such as contact time, and metal ion concentrations refer to the parameters of the prior study. The variables are in a specific range. In addition, the scope of study for contact time, initial copper ions concentration and adsorbent dosages will be in the range of 30minutes, 1-50mg/L and 0.025-0.150grams respectively. For any parameter optimum value not in the specified range should not be accepted and the input data must be adjusted. The objectives one is said to be achieved once the optimum contact time, initial copper ions.

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LITERATURE REVIEW

Adsorption

The process of adsorption, a type of separation process, involves the concentration or agglomeration of one or more gaseous substances or liquids from one phase at the surface of another phase, leading to the completion of the separation process. This process is widely used for the removal of pollutants due to its potential benefits such as cost-effectiveness, simplicity of design, user-friendliness, and low energy requirements [3]. The adsorption process involves two key components: the adsorbent and the adsorbate. The interaction between these two components can be carried out by two adsorption processes, namely physical and chemical adsorption.

Batch adsorption, a traditional yet efficient technique, is employed for the elimination of diverse contaminants from both artificial and natural wastewater [4]. During this process, several parameters, including the concentration of the adsorbate, the dosage of the adsorbent, the duration, and the temperature, are monitored at optimal set points in a specially designed reactor. Once the system reaches an equilibrium state, the adsorbent is removed from the content. Despite its simplicity and relatively lower cost, the batch adsorption process has a significant disadvantage: the pollution load feed is limited to a small amount (limited adsorbate), which makes it rarely used for practical industrial purposes.

Adsorption isotherm models can be used to analyze the interactions between the adsorbate and the adsorbent in batch adsorption. These models help predict the performance of the adsorption process and evaluate the optimization of the process. Table 1 shows the two most common isotherms with their respective linear equations. Adsorption occurs for various reasons, including the deformation of the strength of the adsorbate and the equilibrium forces among particles within the surface of the adsorbent [5].

Table 1. Specifications of batch adsorption models along with their parameters

Batch Adsorption Model	Linear Equation	Parameters of Model
Langmuir Isotherm Model	$\frac{1}{q_e}=\frac{1}{q_m K_L C_e}+\frac{1}{q_m}$	KL(L/mg)
Freundlich Isotherm Model	$log\ q_e = log\ K_F + \frac{1}{n} log\ C_e$	KF(L/mg)

Rice Husks (RH)

Rice, a staple food consumed globally, grows abundantly and rapidly, particularly in Malaysia. The rice husks (RH), a byproduct of rice, are composed of approximately 32% cellulose, a compound that significantly enhances their adsorption capacity [6]. This high cellulose content, coupled with the cost-effectiveness and absence of harmful by-products, makes rice husks a suitable alternative to conventional adsorbents. The morphology of rice husks, characterized by an irregular shape and high porosity, provides active sites for adsorption. The irregular shape increases the surface area available for adsorption, while the porous structure allows pollutants to penetrate and get trapped inside, enhancing the overall adsorption capacity. These attributes make rice husks a promising candidate for green and sustainable adsorption technologies in wastewater treatment.

METHODOLOGY

Utilizing the FAST simulation tool, we model the breakthrough curve with the homogeneous surface diffusion model (HSDM) and its variant, the linear driving force model (LDF). The generation of the breakthrough curve for a fixed-bed system necessitates the predefinition of input parameters. These parameters are divided into two categories: outer and inner model parameter [7]. Outer parameters, indicative of operating conditions, encompass the particle density, diameter, and batch volume. Inner model parameters, which are derived from designed experiments as they cannot be directly measured, consist of the adsorption equilibrium parameters

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(Langmuir n and K_L), film diffusion coefficient (k_L) also referred to as liquid-phase mass transfer coefficient, and the surface diffusion coefficient (D_s), also referred to as the solid-phase mass transfer coefficient.

The initiation of the simulation process involves the selection of the experimental type. For this research study, the column breakthrough experiment type is selected to simulate the breakthrough curve of a continuous fixed-bed adsorption column. The Homogeneous Surface Diffusion Model (faster) is chosen as the model due to its capability to perform calculations in a larger step time. The input values for the parameters under investigation are consolidated in Table 2.

For the adsorption isotherm study, additional parameters need to be determined from the respective kinetic and isotherm models. These include the Langmuir constant (K_L, n), film diffusion coefficient (k_L) and the surface diffusion constant (D_S). The surface diffusion constant can be ascertained by fitting the simulation to the experimental data. Additional compilation of the required parameters is presented in Table 3.

Table 2. Investigated Parameters Vary in Simulation

Parameters	Contact Time (minutes)	Initial Cu (II) Ion Concentration (ppm)	Adsorbent Dosage (grams)
Ranges	0-30	1-50	0.025-0.150

Table 3. Input Parameters and Respective Units

Input Parameters	Values	Unit
Particle Density	116.98	kg/m^3
Particle Diameter	90	µm
Batch Volume	10	mL
Langmuir Max. Loading	1.4	-
Langmuir Constant	1.53	-
Film Diffusion Coefficient	5.5e-6	m/s
Surface Diffusion Coefficient	7.97e-11	m^2/s

RESULTS AND DISCUSSION

Effects of Contact Time

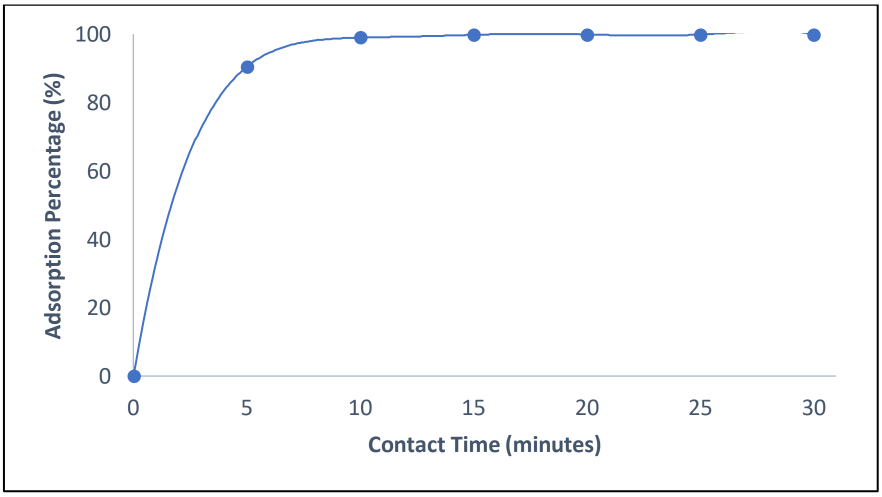

Figure 1. Adsorption Percentage against Contact Time

Figure 1 illustrates the impact of contact time on the percentage of copper ions adsorption. The graph, generated through the FAST simulation run, shows that the adsorption percentage increases with contact time and reaches equilibrium after a certain period. The simulation study reveals that the adsorption process, using RH as an adsorbent, escalates rapidly until 5minutes, with 9.6% of copper ions concentration remaining at the effluent concentration. Then plateaus at 10 minutes, with a maximum adsorption of 99.8% [5].

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The uptake rate of copper ions is substantial at the initial stage due to the abundance of active vacant sites available to capture the copper ions. Initially, all adsorbent surfaces are unoccupied with any metal adsorbate, resulting in a larger surface area of RH adsorbents available for the adsorption of copper ions. As time progresses, the available vacant sites on the RH adsorbent surface become saturated, leading to fewer and limited vacant sites available for new adsorption to occur. The adsorption process gradually reaches equilibrium from 10minutes onwards, with no significant percentage removal observed. Equilibrium is achieved when the adsorption rate equals the desorption rate, or when the removal of adsorbates is no longer significant [2].

Effects of Initial Copper Ions Concentration

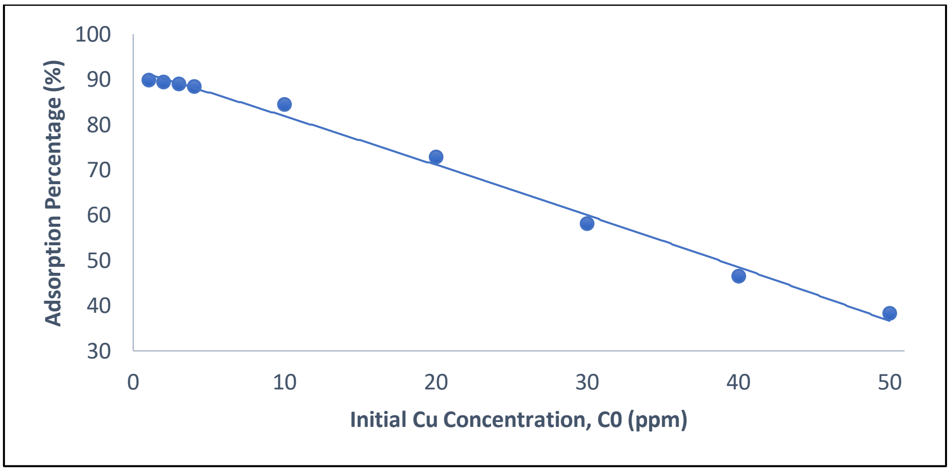

Figure 2. Adsorption Percentage against Initial Cu Concentration

Figure 2 presents the simulated results on the impact of initial copper ion concentration on the percentage of adsorption. The graph indicates that as the initial copper ion concentration increases from 1ppm to 50ppm, the percentage removal decreases from approximately 90% to 38%.

The simulation result from FAST reveals a gradual decrease in the percentage adsorption with an increase in the initial copper ion concentration, suggesting a decrease in the efficiency of copper ions removal by RH adsorbent at higher copper ion concentrations. This trend aligns with several previous experiments where effective adsorbate removal occurs at a lower initial adsorbate concentration [8]. In scenario of low initial copper ion concentration, the ratio of initial moles of copper ions to the available active sites on the adsorbent surface is large. Consequently, the diffusion rate of copper ions towards the RH adsorbent surface increases. However, at high concentrations, the available active sorption sites become fewer and limited, leading to a lower percentage removal that depends on the initial copper ion concentration.

Effects of Adsorbent Dosage

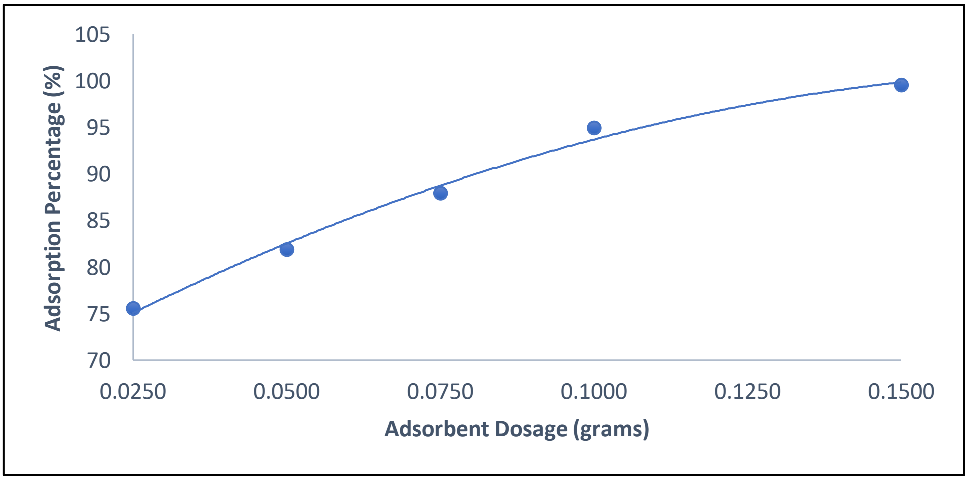

Figure 3. Adsorption Percentage against Adsorbent Dosage

Simulation results, as shown in Figure 4.3, indicate a swift initial adsorption percentage at an adsorbent mass of 0.025grams, with 76% of copper adsorbed. As the dosage of the adsorbent, RH, increases from 0.025grams to 0.15grams, the adsorption percentage gradually increases until equilibrium is reached.

The rise in adsorption percentage is attributed to the increase in adsorbent dosage, which expands the total surface area of the adsorbent in contact with the copper ions solution. This expansion facilitates the penetration and adsorption of copper ions onto the active sorbent sites [8]. Moreover, a higher collision frequency between the adsorbate and the active sites of the adsorbent can be achieved at a high dosage [9]. As equilibrium is approached, the adsorption efficiency slows down and eventually stabilizes, as most of the binding sites become occupied, making it challenging for the remaining adsorbates to interact with the adsorption sites. The maximum adsorption percentage of 99.6% is achieved upon reaching equilibrium where the adsorbent dosage is 0.15grams. This simulation result also suggests that using 0.15grams of rice husk adsorbent dosage is optimal for economic purposes. Any adsorbent dosage beyond 0.15grams will not significantly enhance the percentage of adsorption, leading to unnecessary wastewater treatment costs [10].

CONCLUSION

The adsorption of copper ions onto rice husk (RH) adsorbent was investigated over a period of 60minutes. The highest adsorption of copper ions was observed at 10minutes of contact time, with 99.8% of copper ions removed. At an initial copper ion concentration of 1ppm, the highest adsorption recorded was 90%. The adsorbent dosages used in this research ranged from 0.025grams to 0.15grams. The optimal RH adsorbent dosage was found to be 0.15grams, achieving an adsorption percentage of 99.6%. For the first objective, the optimal contact time, initial copper ions concentration, and adsorbent dosages fell within the range of the study. The second objective, the isotherm study, was also achieved. The simulated results showed that the Langmuir Isotherm was the best fit model to describe copper ions adsorption onto RH, compared to the Freundlich Isotherm. The correlation coefficient of the Langmuir Isotherm in this study was 1.0000, while the Freundlich Isotherm was only 0.9280, verifying the fitness of the Langmuir Isotherm in this study.

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