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Simulation Study of Copper Ions in Wastewater by using Rice Husks Ash

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This study was conducted on the prediction of adsorption capabilities of rice husks ash (RHA) for Copper (II) ions in wastewater solution by simulation study using the Fixed-bed Adsorption Simulation Tool (FAST) software in comparison with its experimental results. FAST simulated the efficiency of RHA as an adsorbent based on parameters of the contact time, Copper (II) ion concentrations, and RHA mass. Two calculation models were adopted using the software to determine the breakthrough curves of rice husks ash as an adsorbent, i.e., Homogeneous Surface Diffusion Model (HSDM) and Linear Diffusion Force (LDF) approximation model. The 2 h of contact time used while employing 10 to 80 ppm of metal concentration and RHA dosages of 5 to 10 g along with this simulation study. The findings have shown that a longer duration of contact time, the higher adsorption rate of copper (II) ions due to the increased possibility of RHA's active sites for metal ions adsorption, corresponds to decreasing metal concentration in final metal ions solutions. The highest adsorption efficiency of 99.81 % was obtained whenever 10 ppm of copper (II) ion concentration was applied as initial metal ion concentration during the experiment. The adsorption rate was higher by increasing the adsorbent mass due to increased RHA active sites for metal ions adsorption at optimum pH 7.

1. Introduction

Recently, Malaysia has overseen a lot of development in industrialization and urbanization. Removing heavy metals waste from industries became the worst scenario especially surrounding the industrial areas where the high possibility the industries discharged heavy metals to water bodies seems beyond the permissible limits, causing wastewater problems. Wastewater streams from electroplating sectors seem to be one of the major pollutants in Malaysia's water bodies nowadays. Wastewater treatment is crucial by using conventional or advanced treatment processes, and one of them is via the adsorption process. The adsorption process is one of the go-to processes for significant industries for heavy metals removal from the wastewater to adhere to regulation final concentration limits that allowable discharged to the environment (Ang and Mohammad, 2020). Experimental and modeling research is getting attention from researchers on finding an efficient method in removing most of the heavy metals by-products (Ang and Mohammad, 2020). Simulation software, namely the Homogeneous surface diffusion model (HSDM), is introduced in this research to predict adsorbent capabilities and integrating the modeling data to a full-scale design for fixed-bed adsorbent (Hand et al., 1984). In this context, the application of the adsorption model used rice husks ash (RHA) as a natural adsorbent for copper (II) ions removal from wastewater by comparing it with its actual experimental data as a basis. The adsorption process is chosen as one of the most used methods to reduce heavy metals concentration in wastewater treatment in this research works.

In contrast, most industries that preferred commercial adsorbent, namely, activated carbons (AC), are commonly used in wastewater treatment while removing toxic inorganic heavy metals ions (Ang and Mohammad, 2020). AC has characteristics of a well-developed porous structure, higher specific surface area, and functional groups (Burakov et al., 2018) that make AC the most popular adsorbent nowadays used for wastewater treatment. Due to RHA as a biosorbent, several experiments have been done to investigate the efficiency of rice husk-based activated carbons as an alternative adsorbent by employing the optimum

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parameters for heavy metal removal in the wastewater (Kumari and Tripathi, 2019). Fewer studies have explored simulating the adsorption process by activated carbons as an adsorbent (Irene and LoPota, 1996). One of the predictive modeling software employed, namely, Fixed-bed Adsorption Simulation Tool (FAST), is used without relying only on the experimental studies (Claudia et al., 2010). With the aid of the software, the viability of the HSDM dynamic model for activated carbon-based adsorbent is investigated as a predictive basis on adsorption rate for rice husks ash as adsorbent (ELTurk et al., 2019). The significance of the study is to develop a mathematical model that corresponds to the simulation study in predicting the rate of adsorption of copper (II) ions by RHA in the actual wastewater. This simulation study referred to the previous research works that only addressed the removal of metal ions in selected pH, metal ions concentration, and selected pH for laboratory works scale (Naeem et al., 2011). It is necessary to find a suitable approach by using FAST as a simulation study due to the limitation of a high concentration of copper (II) in actual wastewater due to the difficulty of handling a high concentration of actual metal ions in laboratory works. This study investigates the efficiency of copper (II) ions removal from metal ions solutions using rice husks ash.

2. Methodology

2.1 Determination of dynamic adsorption process parameters

The mass transfer coefficient of rice husks ash (RHA) was obtained from the previous experimental studies. The value obtained and calculated in average and used in the experimental studies. The heat transfer coefficient for rice husks ash was obtained from the previous experimental studies based on the Freundlich and Langmuir isotherm. The constants and coefficients were observed in the experiment and fitted with linear correlations in finding the Freundlich and Langmuir coefficients.
For kinetic models in FAST, two options are provided to simulate the run for breakthrough curves on rice husks ash as adsorbent, HSDM, and the LDF model. HSDM model requires a few dimensionless parameters from the adsorption mass transfer models, which are Biot number, Stanton number, and surface diffusion model. For the LDF model, the dynamic model is based on the pseudo-first-order model. For adsorption isotherm models, three parameters are being determined from the corresponding kinetic and isotherm models: K, 1/n (isotherm constants), and D_s. K value determines the capacity of the adsorbent, which affects the simulation model error, while 1/n value affects the breakthrough curve shape, which influences the adsorption rate. D_s value is calculated to predict sensitivity of change from any calculated parameters such as the computed effluent concentration.

2.2 Manipulated variables on simulation runs

In FAST, input for the simulation on contact time is recorded in the operational time box in Figure 1. A range of contact time is determined for the simulation of the breakthrough curve (Sperlich et al., 2008). From 5 min until 2 h, the other parameters remained similar. The simulated data run by FAST software (FAST, 2011) and the breakthrough curve is recorded in Microsoft Excel. Recorded data and error analysis from the breakthrough curve were then compared with similar experimental studies.

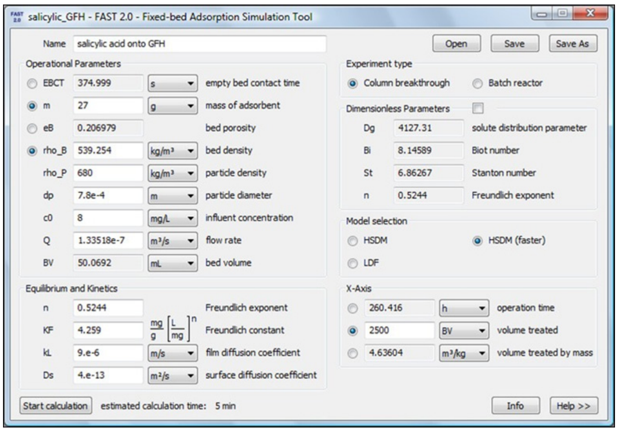

Figure 1: FAST Software

The simulation determines a range of feed metal ions concentration to produce a breakthrough curve. A range of 10-80 ppm feed concentration is run by FAST software, and the breakthrough curve is created again recorded by Microsoft Excel.

A range of mass adsorbent inputs is determined to simulate to produce a breakthrough curve. A range of 5 g to 10 g is being used in the simulation while the other parameters remain similar.

3. Results and discussions

The simulation was conducted to investigate the effect of contact time, metal ions concentration, and adsorbent dosages for copper (II) ions removal from wastewater.

3.1 Effect of contact time

Several variables have remained constant for the simulation of the effect of the contact time. The variables that were remained constant were; the mass of adsorbent, which is 5 g, initial concentration of copper ions in the solution, 40 ppm, RHA density and diameter, which are 2,371 kg/m^3 and 0.074 mm, in values, and the batch volume of the system which is 250 mL at pH of 7. The contact time investigated are 15, 30, 60, 90, and 120 min (Naeem et al., 2011). Based on the simulation using the FAST study, the amount of metal adsorption is increased with the increase of contact time until it reaches equilibrium (Imran et al., 2016). From Figure 2, the simulation study found that the adsorption process increased exponentially until 20 min and then achieved a plateau at 32 min of the contact time.

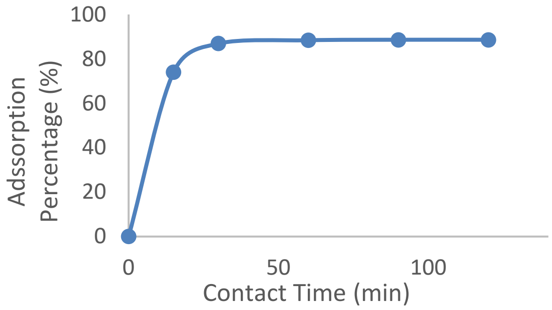

Figure 2: Adsorption percentage vs contact time

In a simulation, 26 % of copper concentration was left at the final concentration in 15 min of operational time. In contrast, in the 30 and 60 min, 13.1 % and 11.6 % of copper ions are left in the solution. At 90 min and 120 min of contact time, 11.4 % of copper ions were found. The maximum adsorption of copper (II) ions by RHA occurred at 32 min and reached maximum adsorption of 90 %, most probably due to maximum adsorption of copper (II) ions onto the available active sites of RHA. The optimum initial concentration of copper used is 40 ppm, the volume of the solution of 250 mL, and copper ions concentration in the metal ions solution is 10 mg, which is used in this adsorption study using rice husks ash for copper (II) ions removal.
In Figure 3, the amount of metal ions adsorbed is rosed with an increase of the contact time by the simulation process of FAST software until it reaches a stagnant value after 35 min of the contact time. It has shown that the amount of copper ion adsorbed increased linearly with the increase of contact time. However, from the linear regression, the value of R^2 is 0.4123, which is too low for the theory to be accepted. The graph representing the amount of copper adsorbed is high before reaching a plateau phase where the amount of copper adsorbed is constant. The data have shown that increasing contact time will increase the amount of the metal ions adsorbed by the adsorbent.

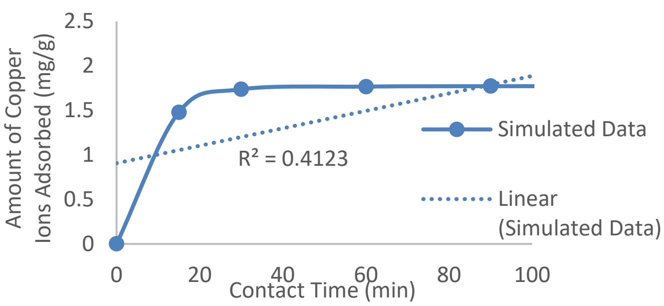

Figure 3: Copper ion adsorbed vs contact time

3.2 Effect of metal ions concentrations in wastewater

For the simulation study of the effect of initial metal ions concentration, 10, 20, 30, 40, 50, 60, 70, and 80 ppm (Naeem et al., 2011) were carried out (Figure 4). Based on the simulation of initial copper ions concentrations, the adsorption percentage gradually decreased indicates less adsorbent efficiency in adsorbing the higher concentration of heavy metals solution (Iftekhar et al., 2018). Theoretically, this is due to the high amount of metal ions species causes more competition of freely metal ions in the solutions to be adsorbed, limited active adsorption sites, and less available to be bounded to the adsorbent. Pre-treatment of high concentrations of feed metal ions solutions is required to reduce the metal concentration, on the other hand, to increase the efficiency of the adsorption process (Ishak et al., 2016).

From Figure 4, 10 ppm of initial metal concentration was achieved 99.81 % of copper ions removal, while for 30 ppm and 50 ppm, it has found that 94.27 % and 82.51 % of copper adsorbed by the rice husks ash. By increasing 70 and 80 ppm of copper ions concentration, only 71.41 % and 66.75 % of copper were adsorbed by the rice husks ash. This finding shows that at 10 ppm is the optimum feed concentration, achieved the optimum of copper (II) ions adsorption. It increases the feed metal ions concentration, and copper efficiency (II) ions adsorption decreases. The amount of metal being adsorbed by the rice husks ash was then calculated, with the adsorption percentage multiplied by an initial amount of copper ions in the solution.

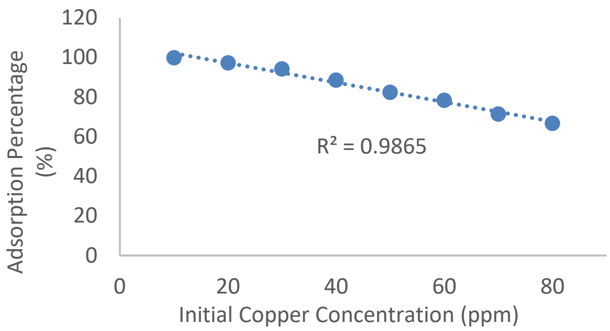

Figure 4: Adsorption percentage vs initial concentration

Figure 5 shows that the amount of metal ions adsorbed is high with increased contact time by the simulation study using FAST software. The data replicate the theoretical explanation that increasing initial copper concentration will increase the amount of the adsorbate being adsorbed by the adsorbent (Acharya et al., 2018). The number of ions adsorbed by rice husks ash based on the adsorbent's maximum adsorption capacity in adsorbing the required metal ions in the solution. The duration taken of metal ions adsorb by RHA increased with the time taken, increasing the efficiency of removing metal ions (Tuas and Masduqi, 2019).

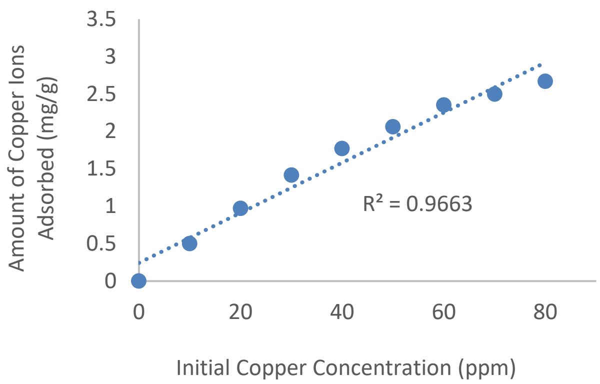

Figure 5: Copper ion adsorbed vs initial concentration

3.3 Effect of adsorbent dosages

For investigation of the effect on RHA dosages, 5, 6, 7, 8, 9, and 10 g were used (Naeem et al., 2011). Based on the FAST simulation, the percentage of metal adsorption increased with the increase of adsorbent. In Figure 6, the adsorption percentage rises gradually, indicating higher adsorbent efficiency of copper (II) ions if using a higher mass adsorbent. Theoretically, with a higher amount of adsorbent used, an increased number of active adsorption sites available for the adsorbent also increased (Guo and Wang, 2019). Based on this research, by increasing the adsorbent dosage, the efficiency in copper (II) ions removal from the metal ions solution will be increased.

In this simulation, 5 g of RHA results from 88.6 % of copper (II) ions being adsorbed, while by using 6 g of adsorbent, 93.5 % and 96.2% of copper (II) ions adsorbed by the rice husks ash. At the range of 9 to10 g of adsorbent, 98.57 % and 99.07 % of copper (II) ions well-adsorbed from the metal ions solutions; by increasing RHA dosages, available sites to adsorb copper (II) ions increased, increasing copper (II) ions removal efficiency.

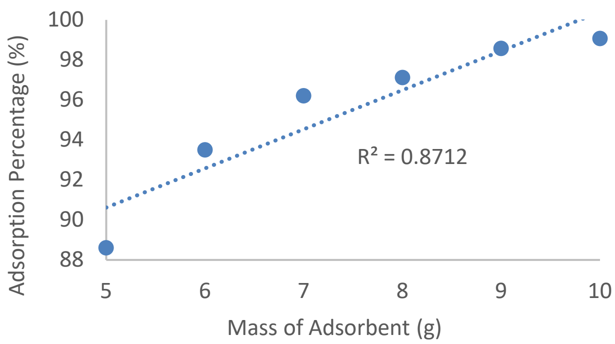

Figure 6: Adsorption percentage vs adsorbent mass

In Figure 7, it has been shown that the amount of metal ions adsorbed is higher by increasing the mass of the adsorbent. The data demonstrated by increasing adsorbent mass, the number of ions adsorbs to the adsorbent's increase due to the maximum adsorption capacity of the adsorbent's space to adsorb metal ions the solutions (Khodami et al., 2017).

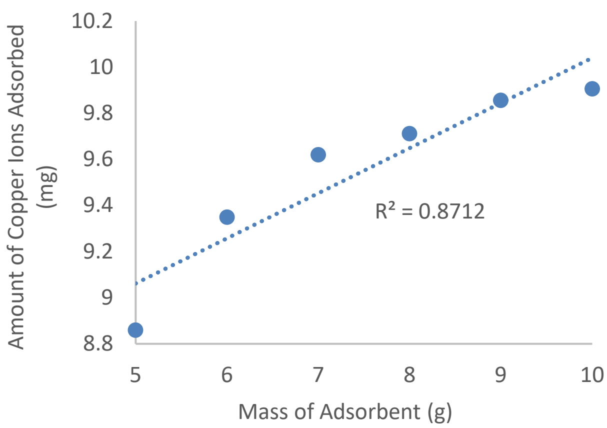

Figure 7: Copper ion adsorbed vs adsorbent mass

4. Conclusion

Rice husks ash (RHA) is a good biosorbent in removing copper (II) ions from the metal ions solutions. The optimum contact time for the highest adsorption of copper (II) ions found at 20 min. The highest efficiency of adsorption showed rice husk ash (RHA) as a biosorbent in removing copper (II) ions from the wastewater. The chemical composition of rice husks promotes RHA's ability to absorb metal ions from the solutions. By burning rice husks into ash, increasing the number of available space of activated carbons, increasing metal ions bonded to the adsorbent surface enhances metal ions' adsorption process. The RHA adsorption of copper (II) ions is good since the efficiency could reach 90% if applied to the optimum tested parameters. The simulation findings, Langmuir isotherm, showed the best fit correlation compared to the Freundlich isotherm predicting the adsorption efficiency in removal copper (II) ions. The simulation data showed by increasing the contact time; adsorption efficiency increased due to the amount of available active adsorption site placed; the metal ions have adequate time to fill in the space of the adsorbent in the solutions. Adsorption efficiency is also higher when the adsorbent dosages increase due to the adsorbent's efficiency by providing an additional active adsorption site. Adsorption efficiency is decreased when the initial concentration of metal ions increased due to the competition of free metal ions to bound to limited adsorbent sites in the metal ions solutions.

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