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Reciprocal effect of variables on the removal of Cu(II) by Fe/Mn-diatomite material

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ABSTRACT

Heavy metal pollution is a major problem in the environment. The impact of toxic metal ions can be minimized by different technologies, viz., chemical precipitation, membrane filtration, oxidation, reverse osmosis, flotation and adsorption. But among them, adsorption was found to be very efficient and common due to the low concentration of metal uptake and economically feasible properties. In this review paper, Fe–Mn binary oxide incorporated into diatomite (Fe/Mn-diatomite) was prepared by a simple coating method , and removal of Cu(II) from aqueous solutions. The effects of three independent variables including initial ion concentration, removal time, and adsorbent dosage were investigated on the maximum adsorption of Cu (II). The optimum conditions for the adsorption of Cu(II) was obtained: 75 ppm of initial ion concentration, 150 min of removal time and 1.5 g/l of adsorbent. The maximum removal efficiencies of Cu(II) was obtained 86.25%. The results showed that Fe/Mn-diatomite was capable of treating copper metal in wastewater.

Keywords: *diatomite, adsorbed Cu^{2+}, Cu(II) removal, adsorption efficiency, adsorption capacity*

1. Introduction

As industry develops, discharge of high concentration metal ion-containing waste from the battery, dye, petrochemical, and mining industries is steadily rising. In recent years, much attention has been drawn to heavy metals contamination because these substances have a detrimental effect on health. Unfortunately, heavy metals were seen in water, soil and wastewater in different parts Vietnam and over the world. Therefore, in order to protect the environment and human health, the removal of heavy metal ions from water is very important. The efficient removal of these toxic compounds from water has attracted considerable attention in the last decades. Up to now, a number of methods, including oxidation, flocculation and sedimentation, membrane separation, adsorption, ion exchange, biological treatment, and chemisorption filtration, have been utilized for the processing of metal wastewater. Among these methods, the adsorption is recognized as one of the most effective pathways in in-depth treating the sewage with low concentrations of metal (Barakat , 2011)

Diatomite ($SiO_2 \cdot nH_2O$) is a sedimentary rock with a porous structure, low conductivity coefficient and low density. It consists essentially of high quantities of silicon dioxide SiO_2 and low quantities of Al_2O_3 and Fe_2O_3 according to the clay impurities. Additionally, the reactivity of diatomite is linked to the reactivity of the hydroxyl groups and the acid sites on the surface of the amorphous silica. Due to its specific characteristics, diatomite has attracted extensive research attention as an adsorbent for its natural and modified structure for the removal of heavy metals, material filtration, catalyst aids, adsorption (Bakr, 2010)

Copper is actually one of the essential minerals for the body under 1 mg/L in drinking water. Copper is necessary for enzymes which are responsible for renewal of body tissue and stability of bone structure. Copper mineral, which plays a role in energy production and protein synthesis, also contributes to the formation of red blood cells. It is essential for nervous system health and is an important mineral in terms of protection of hair and skin health. On the other hand, overdose of copper can lead to serious mental and physical disturbances such as depression, schizophrenia, dementia, hypertension as well as increased risk of cancer. Heavy metals enter to the ecological system by human activities and bio accumulate through food chains and lead carcinogenic effects on human. The sources of copper metal ions at toxic levels are mainly the industrial waste streams of metal cleaning and plating baths, pulp, paper, paperboard and wood preservative-employing mills, the fertilizer industry, etc. (John Kenneth Cruz1 and Leslie Joy Diaz, 2019)

The purpose of this study is to enhance adsorption of copper by supporting Fe/Mn-diatomite material. The effect of Fe/Mn-diatomite material dosage, reaction time and initial copper concentration is also investigated.

2. Arrangement of experiments

2.1. Materials

– Research subjects: Copper solution (Cu^{2+}) (from CuSO4. $5H_2O$ 98% China)

– Research material : Fe/Mn-diatomite material was prepared by Diatomite in Phu Yen province with $FeSO_4$ and $KMnO_4$ appropriate rate (According to Fangfang Chang et all

(2009), Bui Hai Dang Son (2017)).

– Research chemicals: NaOH (China, 96%), HCl (China , 36%), $FeSO_4.7H_2O$ (China, 98%), $KMnO_4$ (China, 99%).

2.2. Arrangement of experiments

Copper ions adsorption studies thirteen batch adsorption experiments were performed at the room temperature to investigate the influence of three independent variables of initial ion concentration, removal time and adsorbent dosage on the ion removal. 100 ml of copper ion solutions with different concentrations poured into Erlenmeyer flask and various amounts of adsorbent were added to the solutions, and stirred with mechanical stirrer in the adjusted agitation speed of 200 rpm. The samples were finally filtered and analyzed by atomic absorption spectroscopy Shimadzu 7000 (AAS) for determining of residual ion concentration, measurement wavelength of 324,8nm.

Experiment 1: According to Fangfang Chang & Jiuhui Qu et all (2009), Ho sy Thang & Pham Dinh Du (2017), Surveying time: 0, 30, 60, 60, 120, 150, 180, 210 minutes, 100ppm concentration, 25ml volume, optimal dosage, optimal pH =.4.

Experiment 2: According to Fangfang Chang & Jiuhui Qu et all (2009), Ho sy Thang & Pham Dinh Du (2017): Dosage survey: 0.2, 0.5, 1, 1.8, 2g/l. 100ppm concentration, optimal pH = 4, time survey: 30, 60, 60, 120, 150, 180, 210 minutes.

Experiment 3: According to Fangfang Chang & Jiuhui Qu et all (2009), Ho sy Thang & Pham Dinh Du (2017): Concentration survey: 25, 50, 75, 100, 150 ppm, Surveying time: 0, 30, 60, 60, 120, 150 minutes, , optimal pH = 4.

2.3. Evaluation methodology

– Copper ions adsorption studies thirteen batch adsorption experimentsn were performed at the room temperature to investigate the influence of three independent variables of initial ion concentration, removal time and adsorbent dosage on the ion removal. 100 ml of copper ion solutions with different concentrations poured into Erlenmeyer flask and various amounts of adsorbent were added to the solutions, and stirred with mechanical stirrer in the adjusted agitation speed of 200 rpm. The samples were finally filtered and analyzed by atomic absorption spectroscopy Shimadzu 7000 (AAS) for determining of residual ion concentration, measurement wavelength of 324,8nm.

– Standard curve method for quantification: 0,1ppm; 0,2ppm; 0,5ppm; 1ppm; 1,5pm; 2ppm.

3. Results and Discussion

3.1. Effect of contact time

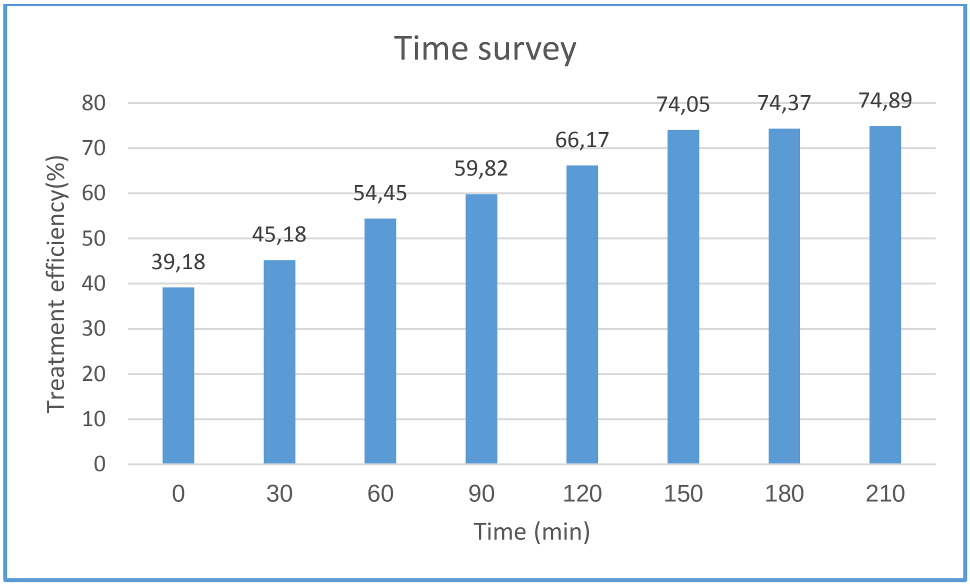

Figure 1. *Result of determining the effect of time on copper metal processing efficiency of Fe/Mn-diatomite*

The research results processing capability of the material Copper metal at pH = 4 is expressed on Fig 1 shows, in the interval of 0, 30, 60, 60, 120, 150, 180, 210 minutes, the performance is as follows: 39,18%; 45,18%; 54,45%; 59,82%; 66,17%; 74,05%; 74,37%; 74,89% . Attraction rapid at an early stage, after 150 minutes, absorption is somewhat increased but not value, path absorption is almost horizontal. Therefore, it can be too hot Cu^{2+} ions reach equilibrium at 150 minutes. Contact time between the adsorbent surface and the adsorbate molecules has a profound effect on the adsorption capacity. Initially when all the adsorbent sites are vacant, the adsorbate molecule adhere to the vacant sites as soon as the metal ions come in contact with them thereby showing a gradual increase in the adsorption with time till a maximum is attained at 150 min as shown in Fig1.

There after no further increase in adsorption is seen which occurs due to fact that when all the adsorbent sites are occupied a dynamic equilibrium is attained in which the number of molecules being adsorbed equals the number of adsorbate molecules being desorbed.

The results of this study are similar to the results of authors Ho Sy Thang and Pham Dinh Du who studied diatomite modification by manganese oxide and copper (II) ion adsorption application in water, the results showed, Adsorption occurs rapidly at the initial stage, after 120 minutes, the capacity increases but not significantly, the absorption capacity line appears to be horizontal.

3.2 Effect of adsorbent Dosage

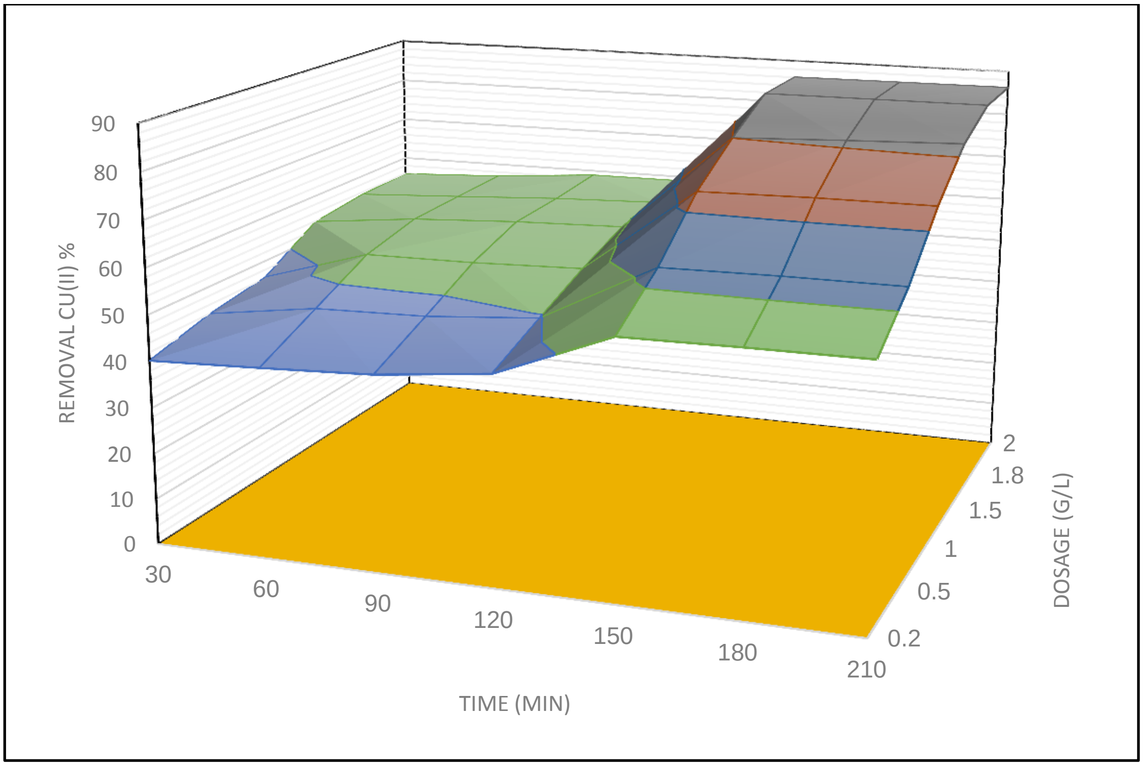

Figure 2. *Response surface, showing the effect of adsorbent dosage on the Cu(II) percentage removal.*

The Combined influence of removal time and adsorbent dosage was analyzed and it was shown in Fig. 2. It can be observed as removal time was increased; the removal efficiency of Cu(II) ion was also increased. The adsorption of ions was fast in the beginning and approached an almost constant value. It implies the achievement of equilibrium. The equilibrium time was obtained at 150 min for Cu(II) ion. Complete removal of ions happened in two separate stages as indicated in Fig 2. The research results capable of processing copper metals at the Fe/Mn-diatomite material at pH = 4 with time: 30, 60, 90, 120, 150, 180, 210 is expressed on Fig 2 shows, in the range of doses of 0.2, 0.5, 1, 1.5, 1.8, 2 g/l has the increasing performance from 54,69% to 86,19%.

During treatment at 1.5g/l, the treatment efficiency was high at 94.53% when increasing the dosage to 2g/l, the saturation adsorption capacity. The study shows that the optimal metal treatment dose is 1.5 g/l with a processing efficiency of 81,83%.

Maximum Cu(II) removal percentage was obtained when there is increasing in adsorbent dosage. By increasing of adsorbent dosage, the removal efficiency of ion was increased due to that activated surface of adsorbent possess more adsorption sites available for ions removal from the solution (John Kenneth Cruz1 and Leslie Joy Diaz, 2019). The decrease in Cu(II) percentage removal with the increase of the ion concentration may be due to the restriction of adsorption sites present on the surface of Fe/Mn-diatomite.

3.3. Effect of initial concentration

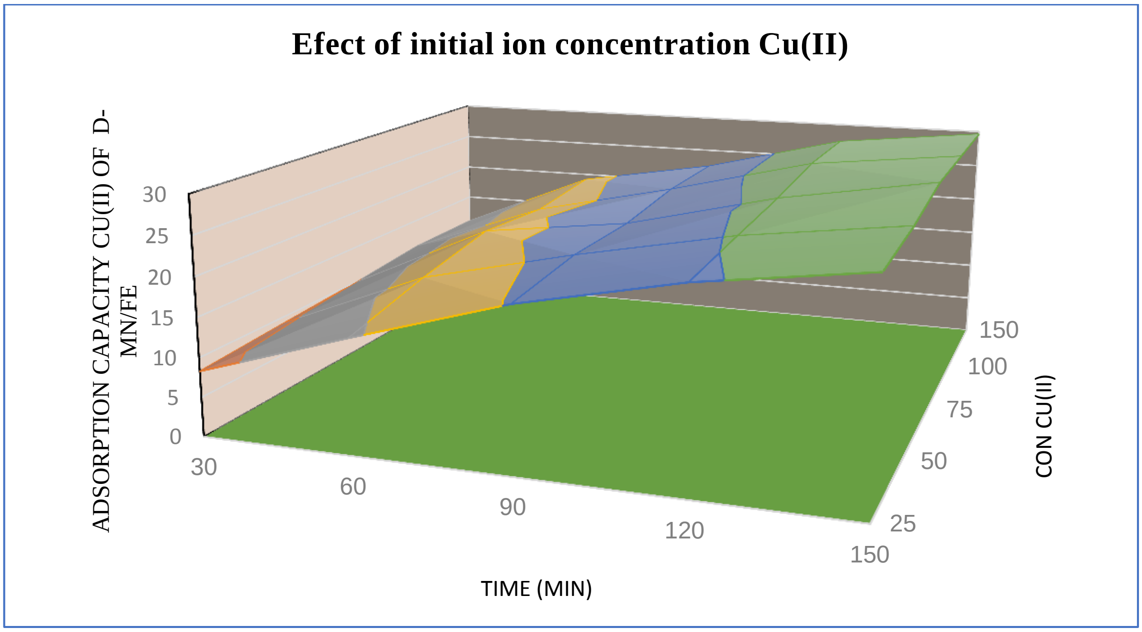

Figure 3. *Response surface, showing the effect of initial ion concentration, removal time and adsorbent dosage on the Cu(II) percentage removal.*

Initial concentration of the adsorbate molecules affects the rate of adsorption to a great extent as depicted in Fig.3. It indicates the effect of two variables on the removal of Cu(II) ion from aqueous solutions. The results indicated that initial ion concentration and removal time have a strong effect on the adsorption capacity of Fe/Mn-diatomite. As can be seen with increasing the initial ion concentration the percentage removal of Cu(II) was increased, for example, when Cu(II) concentration enhanced from 25 mg/L to 150 mg/L, the amount of copper metal ion adsorbed at equilibrium increased from 27,25 mg/g to 29,61 mg/g.

At the lower initial adsorbate concentration lesser number of collisions occur between the adsorbate molecules and the adsorbent which increase with increase in the initial adsorbate concentration and shows sharp increase in the adsorption capacity up to initial concentration of 75 ppm for Cu(II) ion. There is no further increase in adsorption with increasing initial ion concentration due to attainment of the dynamic equilibrium between free adsorbate ions in solution and adsorbed metal ions.

The results of this study are lower than the results of authors Ho Sy Thang and Pham Dinh Du who studied diatomite modification by manganese oxide and copper (II) ion adsorption application in water, the results showed, adsorption capacity of Mn-Diatomite material 36,90 mg/g. Though the comparison is only relative due to the thing research conditions vary, but this also suggests Cu(II) removal of Fe/Mn-diatomite material.

4. Conclusion

This research has explained the probability of response surface Fe/Mn-diatomite material in the effect of three variable parameters on the Cu(II) removal from aqueous solution. Experiments were carried out based on three independent variables included of initial ion concentration, removal time and adsorbent dosage. The results show Fe/Mn-diatomite is good adsorbent for elimination of copper ion and had highly removal efficiency for studying ion.

The optimum conditions for the adsorption of Cu(II) were obtained 75 mg/L of initial ion concentration, 150 minutes removal time and 1.5 g/l of adsorbent.

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