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Adsorption of Copper (II) Ions from Aqueous Solution onto Marble Waste

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ABSTRACT

The presence of heavy metals in the environment is a major concern due to their toxicity for many life forms. This research studied the ability of using Marble Waste (MW) as an adsorbent for the removal of Cu (II) ions from aqueous solution by batch operation. Experimental investigations of a number of operating parameters were performed to assess their effect on the removal of Cu (II) by Marble waste from synthetic solutions. These parameters are contact time, adsorbent dose initial concentration of adsorbate, agitation rate, solution temperature and pH level. The optimum conditions were determined to be pH 6, 2g adsorbent dose, 100 min contact time, 50ppm Cu and 35 ^{0}C for copper removal, and particle diameter at 0.275 μm. The adsorption process of copper (II) is tested with Langmuir and Freundlich adsorption isotherm models. The results revealed that copper is considerably adsorbed on Marble Waste and it could be economic method for the removal of copper from aqueous solutions. Moreover this study gives a value added utilization of biomass to remove Cu from wastewater.

***Keywords**:*
Adsorption.
Heavy metals.
Wastewater.
Langmuir, Freundlich isotherm models.

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1 INTRODUCTION :

The contamination of fresh waters with a wide range of pollutants has become a matter of great concern over the last few decades [1]. The discharge of high amounts of heavy metals into water bodies leads to several environmental and health impacts [2]. Various heavy metals such as copper (Cu), cadmium (Cd), lead (Pb), arsenic (As), zinc (Zn), chromium (Cr), and thallium (Tl) have been released into the environments due to a rapid population growth, development of social economy, industry activities, smelting and mining operations, waste disposal, and the extensive application of pesticides and chemical fertilizers in agriculture.

These metals were reported to be highly toxic even at trace concentration [3, 4]. Copper is a natural element with a widespread distribution, however, exposure to excessive amounts can cause serious health problems because of its bio-accumulation and toxic effects [5]. Copper (Cu) also is a metal that is widely used in industry and it is an essential element in human health. However, like all heavy metals, it is potentially toxic [6]. Heavy metals can be removed by different methods including physico-chemical processes, chemical/electro-chemicalprocesses, coagulation/flocculation, ion exchange, membrane filtration, and biological sorption [7]. The adsorption process by the chelating characteristics of adsorbents is arguably one of the best techniques for elimination of heavy metals which has attracted significant notice because of simplicity, inexpensive, effectiveness and flexibility in design and action [8]. It is very important to find an economically feasible, simple to operate, efficient and sustainable treatment method in order to protect our surface water bodies, eventually our health from heavy metals contamination. In this work, the feasible technical of low-cost and eco-friendly adsorbent material which is marble waste MW, that produced from the marble industry to remove copper ions from contaminated water has been investigated. The results show the removal performance was success and active. The aim of the study was to investigate the efficiency and the practical applicability of locally abundant low-cost adsorbents which was marble waste MW for the removal of copper ions from aqueous solution. In addition, some isotherms have been used to obtain experimental data as well as the investigation of kinetics gives a concept about the mechanism of the adsorption reactions.

2 MATERIALS AND METHODS

2.1 Preparation of adsorbent

Marble waste was collected from marble manufacturing factory in Zliten, Libya. MW was washed thoroughly with double distilled water and then dried in an air oven at 400 ^oC for 24 hrs then grounded and sieved through mesh to obtain desired size fraction using a conventional sieve-shaker (WiseVen) oven.

2.2 Preparation of adsorbate

Standard solution (1000 *ppm*) of copper Cu (II) was prepared by dissolving 3.935g of $\boldsymbol{Cu\,SO_4.5H_2O}$ in 1000 *mL* of distilled water and then was mixed gradually. The required concentration of aqueous solution was prepared from stock solution. HCL and NaOH were used to adjusted pH values of samples, ammonia was used as reagent. In all experimental work, distilled water is used. Furthermore, to prepare required concentration such as 100 *ppm* 50 *ml* of 1000 *ppm* standard solution was taken and diluted to 500 *ml* in a volumetric flask by distilled water with mixing.

2.3 Adsorption Procedures

The general technique that used for this study was described as follows:

A known weight of MW adsorbent (e.g. 1g adsorbent) was equilibrated with 100 *ml* containing known concentration of Cu (II) solutions (50,100,300,500,800 and 1000 *ppm*). These solutions are filtered by using (FILTER-LAB) paper Cod. PN1248110. Then will be adding 3*ml* of ammonia and the concentrations of residual Cu (II) were measured using spectrophotometer equipment (JENWAY 7305 Spectrophotometer) at selected wavelength λ = 610 *nm*. The effect of several parameters such as pH, initial concentrations, temperature, agitation rate, adsorbent dose and contact time on the adsorption were studied. The experiments carried out to identify the optimum conditions for adsorption process. Adsorption experiments were conducted by varying contact time, adsorbent dose, initial concentration of adsorbate, agitation rate, particle size of adsorbent and temperature.

3 RESULTS AND DISCUSSION

3.1 Effect of Contact Time Variation

The process was carried out at contact time interval between 0 to 120 min (0, 20, 30,45,60, 100 and 120min). The removal percentage of Cu (II) from the tanning solution was investigated using 100 ml with a known concentration of Cu (II) solutions (50, 100,300,500 ,800 and 1000 *ppm*) using 400 rpm as an agitation rate, 2g as an adsorbent dose with a particle size of 0.275 µm, a pH of 6 and a temperature of 35 ^{O}C.

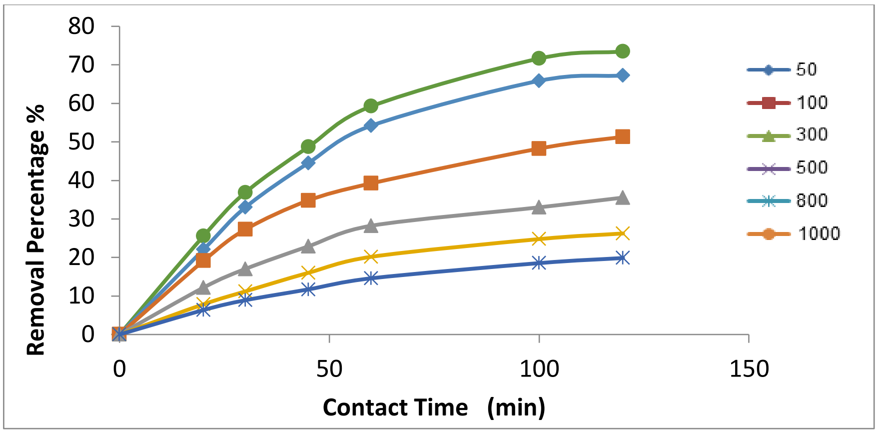

Figure 1. Effect of contact time variation on removal percentage of Cu (II)

Results in figure 1 indicate that, percentage of removal of Cu (II) from wastewater increases as the contact time increases until the equilibrium had been touched, where the equilibrium was started to reach after 100 *min*.

3.2 Effect of Adsorbent Dose Variation

The effect of the amount of adsorbents on adsorption of Cu (II) was studied under constant conditions of contact time of 100 *min* at 400 *rpm*, for 100 *ml* containing known concentration of Cu (II) solutions (50 to 1000 *ppm*), solutions pH at 6, temperature at 35 ^{O}C and the particle size is 0.275 µm, where the mass of adsorbents were changed from 0.5 to 3 *gram* (0.5, 1, 2 and 3).

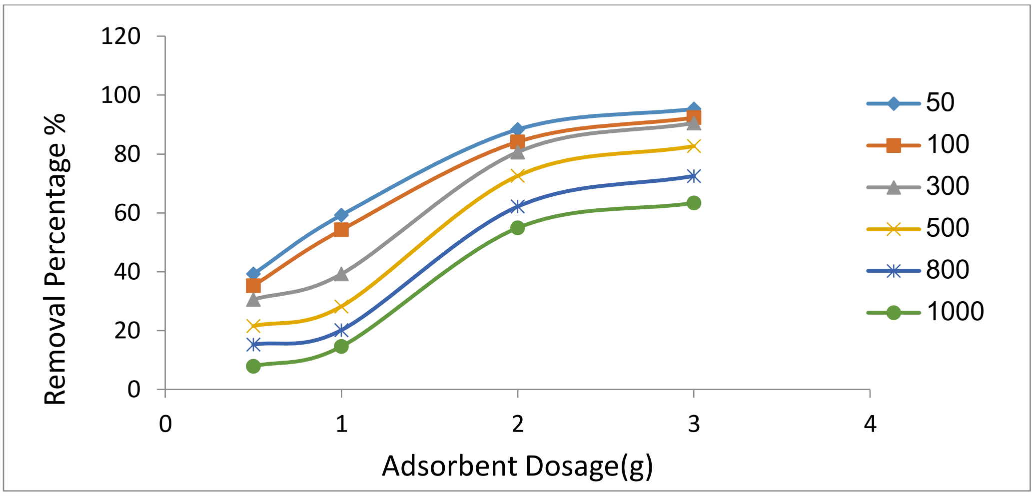

Figure 2. Effect of Adsorbent Dose variation on removal percentage of Cu (II)

The results shown in the figure 2 indicate that the removal percentage of Cu (II) increases with an increase in adsorbent dose. This is due to increase the surface area of MW and hence more active sites are available for the adsorption of more Cu (II) ions.

3.3 Effect of Initial Concentration Variation

The effect of initial Cu (II) ion concentrations on the adsorption efficiency of MW is shown in figure 3. Adsorption experiments were carried out at different initial Cu (II) concentrations ranging from 50 to 1000 *ppm* (50, 100, 300, 500, 800 and 1000) for 100 *min* at 400 *rpm* with 2 *g*/100 ml of solution were used, solutions pH at 6, and temperature at 35 ^{O}C and the particle size is (0.275) µm.

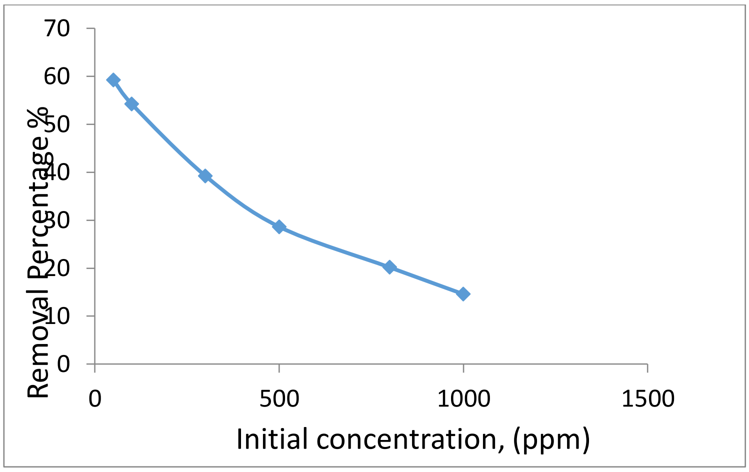

Figure 3. Effect of Initial Concentration on removal percentage of Cu (II)

From figure 3. It was observed as a general trend that there was decrease of the removal percentage with increase in initial concentration.

3.4 Effect of Agitation Rate Variation

The effect of agitation rate on Cu (II) removal from 100 ml of tanning solutions is based on agitation rates of 100, 300, 400 and 500 *rpm* using 2*g* of MW of particle size (0.275) µm at temperature 35 ^{O}C, initial pH of 6 and 100 minutes contact time.

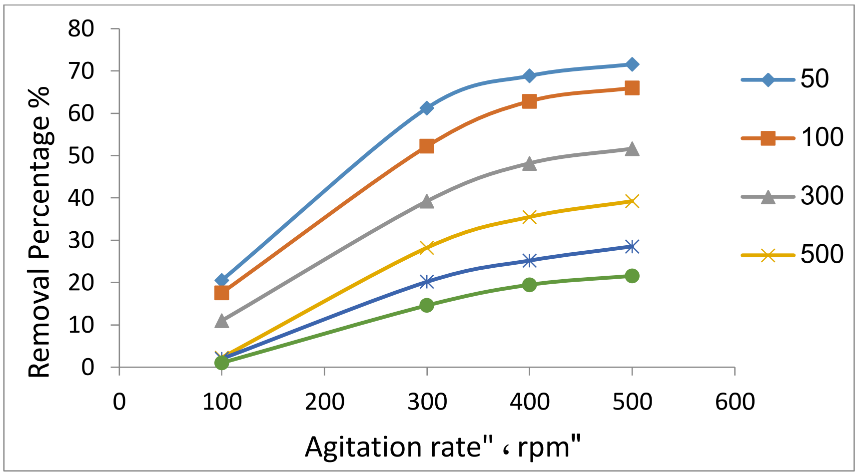

Figure 4. Effect of agitation rate variation on removal percentage of Cu (II).

Results in figure 4 show that, the removal percentage of Cu (II) from wastewater increases as the agitation rate increases. The results reveal that the optimum agitation rate is 400*rpm*.

3.5 Effect of Particle Size

particle size effect on the adsorption of Cu (II) from 100*ml* of solutions containing known concentration of Cu (II) solutions (50, 100, 300, 500 , 800 and 1000 *ppm*) are investigated using 400 *rpm* agitation rate, 2 *g* of MW, temperature at 35 ^{O}C, initial pH equal to 6 and 100 minutes contact time for particle size 0.275 , 0.315 and 0.5µm.

Figure 5 show the plot of the percentage of the metal ions removed against the particle sizes of the adsorbent. From the plots, it was observed that the removal percentage decreases as particle size increases.

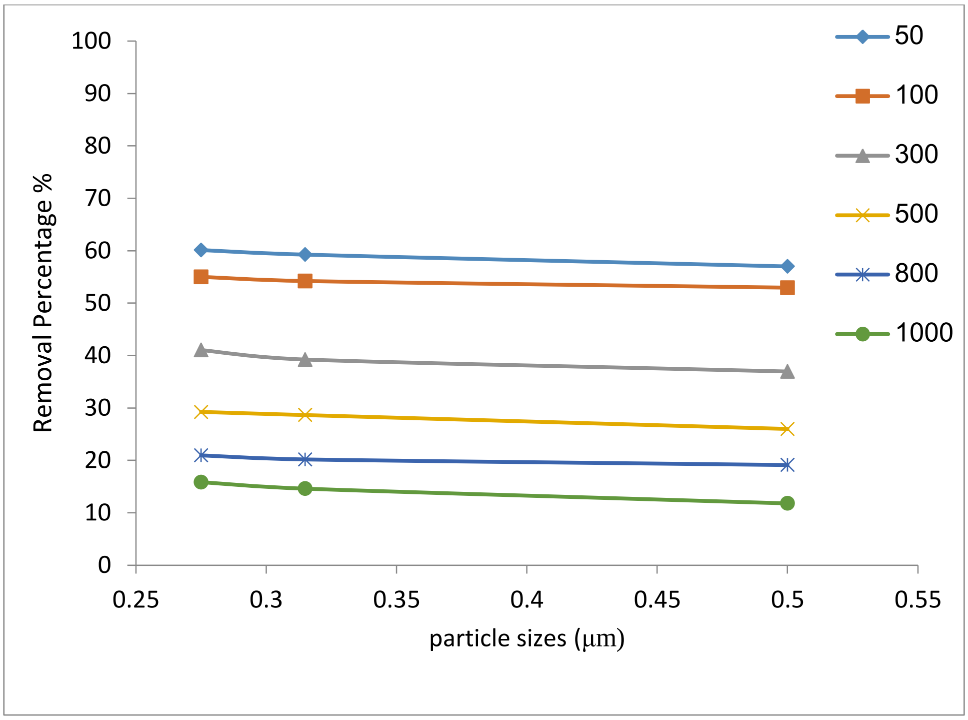

Figure 5. Effect of particle sizes variation on removal percentage of Cu (II)

3.6 Effect of Temperature

Temperature effect on the adsorption of Cu (II) from 100*ml* of solutions containing known concentration of Cu (II) solutions (50, 100, 300, 500 ,800 and 1000 *ppm*) are investigated using 400 *rpm* agitation rate, 2 *g* of MW of 0.275 µm particle size, an initial pH equal to 6 and 100 minutes contact time for 25,35, 45 and 65 ^{O}C. The results in figure 6 show that the removal percentage increases as temperature increases as an indication that the process in endothermic in nature.

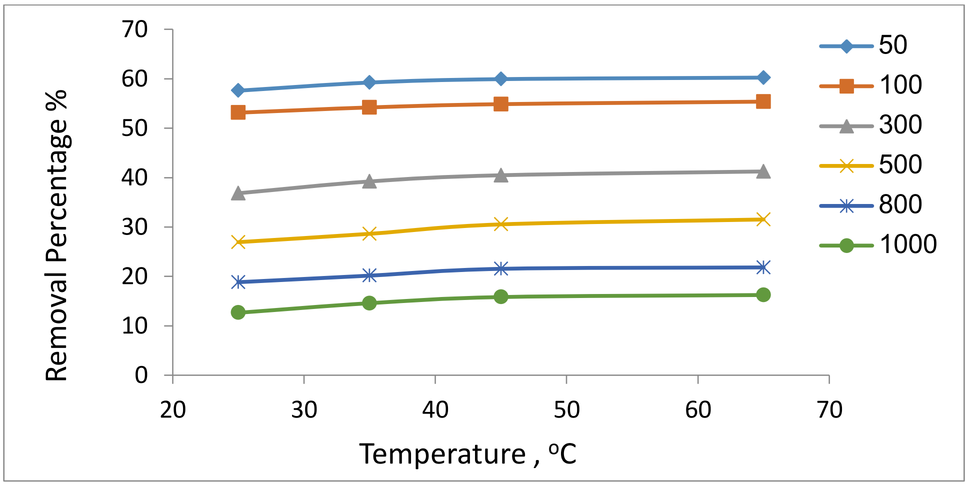

Figure 6. Effect of temperature variation on removal percentage of Cu (II)

3.7 Effect of pH

The pH of solution is considered one of the major factors effecting the adsorption process using MW. Hence, influence of initial solution pH on removal of copper ions from aqueous solution was studied. This study was carried out under constant conditions of contact time of 100 *min* at 400 *rpm* for 100 *ml* containing known concentration of Cu (II) solutions (50, 100, 300, 500, 800 and 1000) *ppm*, 2 *g* of MW of (0.275) µm particle size and temperature at 35 ^{O}C and the solution pH from 4 to 7 (4, 5, 6 and 7). As presented in figure 7 increase of pH from 4 to 6 leading to increases to the amount of copper adsorption. The variation in the amount of adsorption clearly indicated the influence of pH on adsorption process.

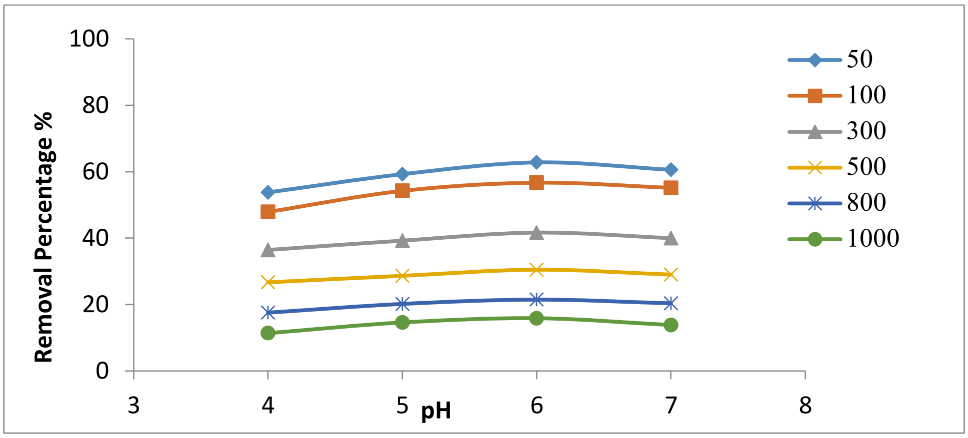

Figure 7. Effect of pH variation on removal percentage of Cu (II).

3.8 Adsorption Kinetics

The kinetics of adsorption was studied for for 100 *ml* containing known concentration of Cu (II) solutions 500 *ppm* at contact time ranging 20-45 min (20, 30 and 45). The experimental data was fitted to the pseudo first order and pseudo second order kinetic model by using equations 1 and 2 to Figure 8 and Figure 9 respectively.

$$\ln(q_e - q_t) = -K_1 t + \ln(q_e) \qquad (1)$$

$$\frac{t}{q_t} = \frac{1}{K_2 * q_e^2} + \frac{t}{q_e} \qquad (2)$$

The reported R^2 value indicates that the experimental results shows better fit to pseudo second order model. Hence, the copper adsorption seems to be more pseudo second order.

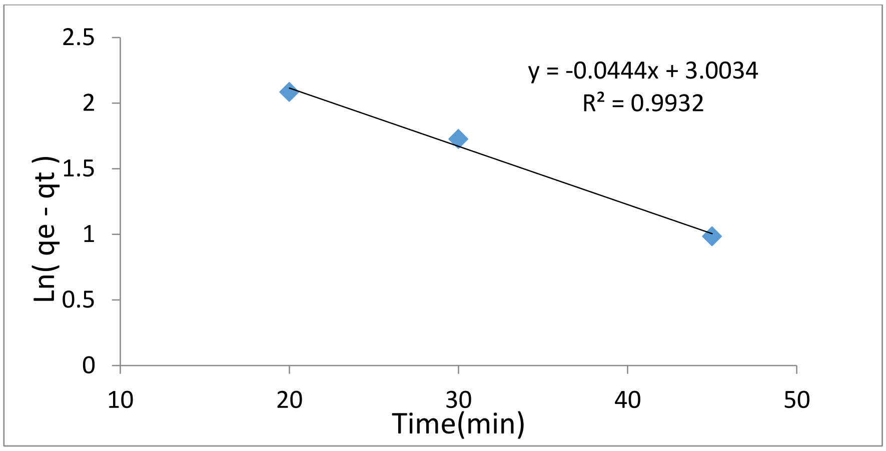

Figure 8. Pseudo First Order Kinetics Plot For Cu (II) Adsorption.

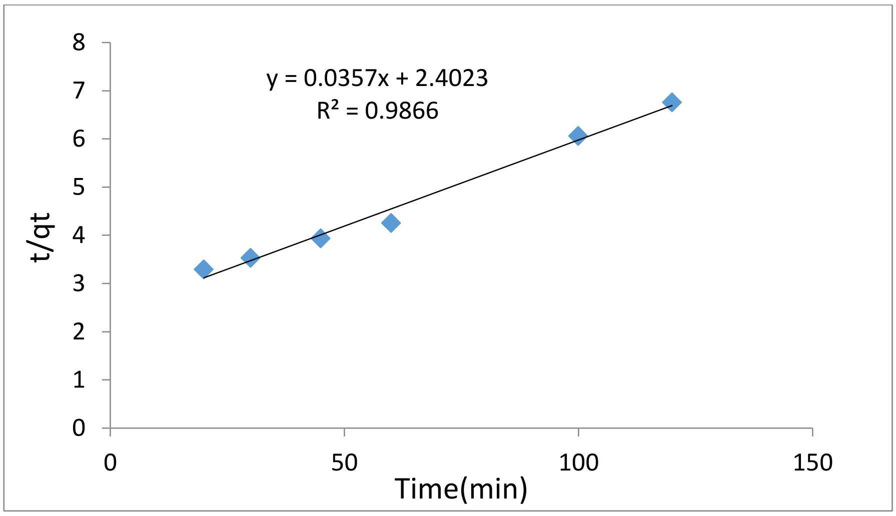

Figure 9. Pseudo Second Order Kinetics Plot For Cu (II) Adsorption.

3.9 Adsorption Isotherm

The adsorption isotherm was investigated for copper removal to evaluate the applicability of adsorption processes as a unit operation and find the relation between metal concentrations in the liquid phase with metal concentration in solid phase at the equilibrium. In order to study the adsorption isotherm of Cu (II) on studied adsorbent, the experimental adsorption data that observed under conditions same conditions of effect of initial concentration was fitted to Langmuir and Freundlich models. Figure 10 and Figure 11 show the plots of Langmuir model and Freundlich model using Eqs 3 and 4 respectively, for removal of copper.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (3)$$

$$\ln(qe) = \ln K_F + \frac{1}{n}\ln Ce \quad (4)$$

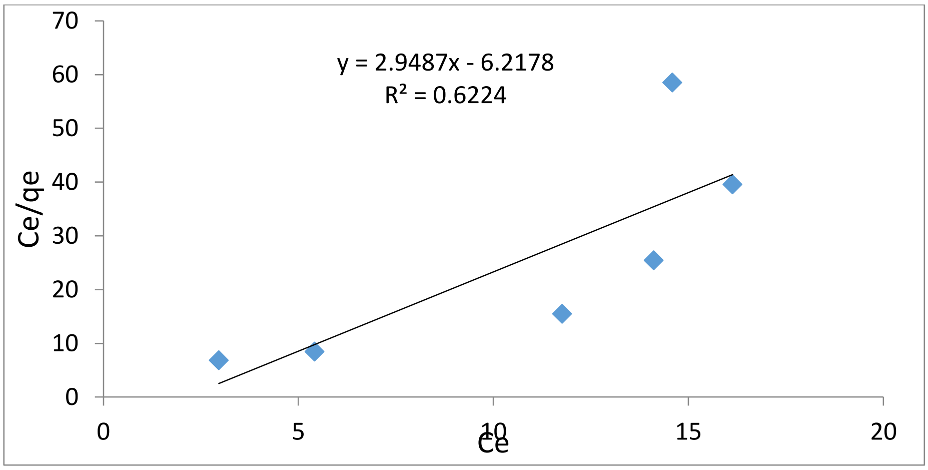

Figure 10. Langmuir adsorption isotherm for Cu (II) adsorption

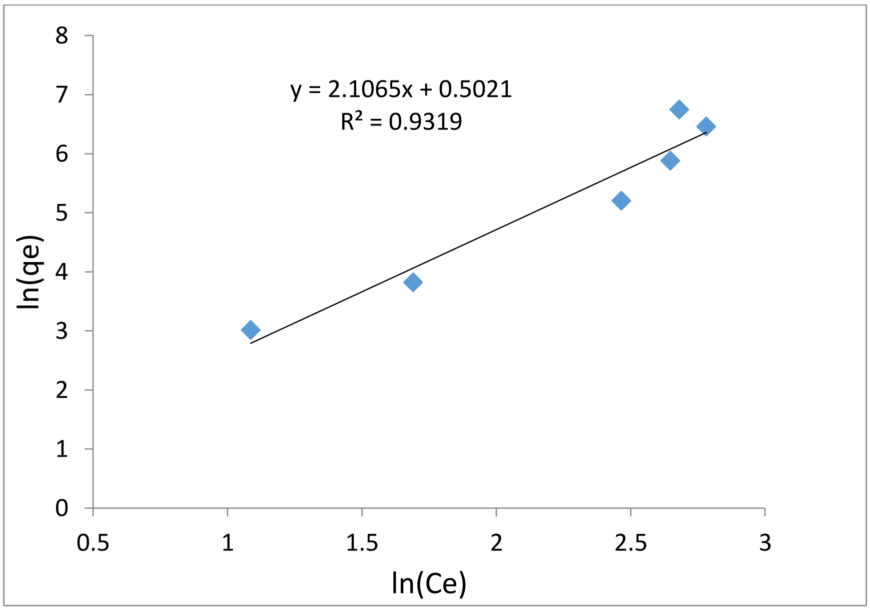

Figure 11. Freundlich adsorption isotherm for Cu (II) adsorption

It indicates that the experimental data fitted well to all the isotherm models. By comparing the correlation coefficients, it was observed that Freundlich isotherm gives a good model for the adsorption system.

4 CONCLUSIONS

The main objective of this research was to study the feasibility and the efficiency of low cost waste materials in the removal of copper (II) ions from wastewater based on adsorption process. MW has been used successfully as an adsorbing agent for the removal of copper (II) from aqueous solutions, the adsorption was influenced by various parameters. The present research indicates to the amount of Cu (II) ions adsorbed on the MW. The optimum pH was found as pH 6 for removal of Cu (II) ions by MW at 35 ^{o}C. On increasing the adsorbent dosage, the adsorption percentage also increases. The optimum contact time for efficient removal was 100 min. kinetic studies of adsorption revealed that the adsorption process followed a pseudo first order kinetic model and data were fitted to different isotherm model equation and the freundlich model was found to be the best model for the adsorption of copper**.**

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امتزاز أيونات النحاس الثنائي من المحاليل المائية باستخدام مخلفات الرخام

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الملخص

الكلمات الدالة:
الامتزاز.
المعادن الثقيلة.
المياه الملوثة.
نموذج فريندلش ونموذج.
لانجماير.

يعد وجود المعادن الثقيلة في البيئة مصدر قلق كبير بسبب سميتها للعديد من أشكال الحياة. حيث درس هذا البحث قدرة استخدام مخلفات الرخام (MW) كمادة مازة لإزالة أيونات النحاس (II) من المحلول المائي بالتشغيل الدفعي. وقد تم إجراء تحقيقات تجريبية لعدد من معاملات التشغيل لتقييم تأثيرها على إزالة أيونات النحاس (II) بواسطة نفايات الرخام من المحاليل الاصطناعية. هذه المعاملات هي زمن التلامس، والتركيز الأولي لجرعة الممتزات ، ومعدل عدد اللفات ، ودرجة حرارة المحلول، ومستوى الأس الهيدروجيني. وتم تحديد الظروف المثلى لتكون الأس الهيدروجيني 6 ، جرعة ممتصة 2 جرام ، 60 دقيقة من زمن التلامس ، 50 جزء في المليون من النحاس و 35 درجة مئوية لإزالة النحاس ، وقطر الجسيمات عند 0.275 ميكرومتر. وتم اختبار عملية امتزاز أيونات النحاس (II) بنماذج متساوية الامتزاز Langmuir و Freundlich. أظهرت النتائج أن النحاس يمتص بشكل كبير على نفايات الرخام ويمكن أن يكون طريقة اقتصادية لإزالة النحاس من المحاليل المائية. علاوة على ذلك، وتعطي هذه الدراسة قيمة مضافة لاستخدام الكتلة الحيوية لإزالة النحاس من مياه الصرف الصحي.

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