Libyan Journal of Ecological & Environmental Sciences and Technology
(LJEEST)
LJEEST
www.srcest.org.ly/jou

DOI: https://doi.org/10.63359/a904qy57

Removal of Copper (II) Ions from Aqueous Solution Using Pine Activated Carbon

Khaled S. Aljfairi[1], Jmal Khlifa Alfeluo[2], Mohannad Abd Alnabi[1]

ARTICLE INFO

Vol. 1 No. 1 June, 2019

Pages (47 - 54)

Article history:
Revised form 02 Mayy 2019
Accepted 01 June, 2019

Authors affiliation
1. Chemical Engineering Department, Al-Asmariya University, Zliten, Libya.
2. Department of Chemical and Petroleum Engineering, El-Mergib University, AlKhoms, Libya
k.aljfairi@asmarya.edu.ly

Keywords:
Wastewater treatment; Adsorption; Activated carbon; Langmuir, and Freundlich isotherm models.

ABSTRACT

The discharge of high amounts of heavy metals into water bodies leads to several environmental and health impacts. To help mitigate the negative impacts of heavy metals (such as copper ions) on the humans and animals health as well as finding of a variety processes to remediate the environment. Adsorption is an essential process that can be applied in wastewater treatment. This work aims to investigate the removal of copper ions (II) from aqueous solutions using low-cost and eco-friendly material such as activated carbon (AC). Thermal activated carbon was prepared from Pine trees. The adsorption of Cu (II) ions from aqueous solutions onto Activated Carbon (AC) was investigated. The experiments were performed in a batch system, at room temperature (20 ± 0.5 °C), and the copper ions analysis was done after equilibrium was attained. Different experimental parameters (initial Cu (II) concentration, pH, sorbent dosage, and contact time) were varied in order to establish the optimum conditions for copper removal using AC. The experimental results were fitted using the Langmuir, and Freundlich isotherm models, and the characteristic adsorption parameters were determined. Experimental data were also tested using two kinetic models: the pseudo-first-order model and the pseudo-second-order model. Based on these models, the kinetic parameters (rate constant and equilibrium adsorption capacity) for Cu (II) adsorption on AC were calculated.

إزالة أيونات النحاس (II) من المحلول المائي باستخدام الكربون المنشط بالصنوبر

خالد صالح الجفيري، جمال خليفة الفلو، مهند عبد النبي

يؤدي تصريف كميات كبيرة من المعادن الثقيلة إلى المسطحات المائية إلى العديد من الآثار البيئية والصحية. للمساعدة في التخفيف من الآثار السلبية للمعادن الثقيلة (مثل أيونات النحاس) على صحة البشر والحيوانات وكذلك البيئة ، توجد مجموعة متنوعة من عمليات المعالجة. الامتزاز هو عملية أساسية يمكن تطبيقها في معالجة المياه العادمة. يهدف هذا العمل إلى التحقيق في إزالة أيونات النحاس الثنائية (II) من المحاليل المائية باستخدام مواد منخفضة التكلفة وصديقة للبيئة مثل الكربون المنشط (AC). تم إعداد الكربون المنشط الحراري من أشجار الصنوبر. وتم فحص امتصاص أيونات النحاس (II) من المحاليل المائية على الكربون المنشط (AC). تم إجراء التجارب في نظام الدُفعات ، عند درجة حرارة الغرفة (20 ± 0.5 درجة مئوية) ، وتم إجراء تحليل أيونات النحاس بعد تحقيق التوازن. تباينت المعاملات التجريبية المختلفة (تركيز (Cu (II الأولي ، ودرجة الحموضة ، والجرعة الماصة ، ووقت الاتصال) من أجل تحديد الظروف المثلى لإزالة النحاس باستخدام AC تم دراسة الإتزان الحراري للنظامين باستخدام نموذجي فريندليش و لانجماير، وتم تحديد معلمات الامتزاز المميزة. تم اختبار البيانات التجريبية أيضًا باستخدام نموذجين حركيين. استنادا إلى هذه النماذج ، تم حساب المعلمات الحركية (معدل ثابت وقدرة الامتزاز التوازن) لامتصاص Cu (II) على الكربون المنشط.

INTRODUCTION

Recently the most significant issues encountering mankind is environmental pollution (Aydın, et al., 2008). This issue grew dramatically until reached the worrying levels in its effects on life on the Earth (Demirbas¸ et al., 2009). From all pollutants the heavy metals are considered the worst because their direct effect on human being and animals (Feng, et al., 2009). Heavy metals including lead, copper, cadmium and chromium, etc. permeate from industrial wastewater leading the groundwater contamination (Kadirvelu, et al., 2001). The activities that responsible for polluting water by heavy metals are some industrial process, domestic and commercial uses (Wan, et al., 2010). Among all treatments of wastewater, adsorption technique is providing a low cost, requires low maintenance and is energy efficient (Li, et al., 2010). In this study, the new and feasible technical of low-cost and eco-friendly adsorbent material which is activated carbon from Pine trees to remove copper from contaminated water has been investigated. Surprisingly, 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 activated carbon that prepared from Pine trees for the removal of copper 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.

MATERIALS AND METHODS

Chemicals

The solutions of Cu^{+2} were prepared by dissolving accurately weighted amounts of $CuN_2O_6.3H_2O$ in distilled water. *HCl* and *NaOH* were used to adjust pH values of samples, ammonia was used as reagent. In all experimental work, distilled water was used.

Preparation of AC

In this study, Pine Coal was used as adsorbent. For using this adsorbent in adsorption experimental, Pine Coal was collected then dried in an air oven at 120℃ for 24 hrs then grounded and sieved through mesh to obtain desired size fraction using a conventional sieve-shaker (WiseVen) oven.

Preparation of Copper Stock Solution

In this work, all chemicals used were of analytical grade. Standard solution (500 *ppm*) of copper was prepared by dissolving 1.901g of $CuN_2O_6.3H_2O$ in 1000 *ml* of distilled water and then was mixed slowly .

In addition, to prepare required concentration such as 100 *ppm*, 200 *ml* of 500 *ppm* standard solution was taken and diluted to 1000 *ml* in a volumetric flask by distilled water with mixing.

Batch Mode Adsorption Experimental Studies

The adsorption of heavy metals on Pine Coal was studied by batch technique. The general method used for this study was described as follow:

A known weight of AC adsorbent (e.g. 1 *g* adsorbent) was equilibrated with 100 *ml* containing known concentration of *Cu (II)* solutions. (25, 50, 75, 100 and 150 *ppm*). These solutions were filtered using (FILTER-LAB) paper Cod. PN1248110. Then 5 *ml* of ammonia was added and the concentrations of residual *Cu (II)* were measured using spectrophotometer equipment (JENWAY 7305 Spectrophotometer) at selected wavelength λ_{max} = 615 *nm* (Demirbas¸ et al., 2009). The effect of several parameters including pH, initial concentrations, temperature, agitation rate, adsorbent dose, particle size and contact time on the adsorption were studied.

Laboratory Studies

Experimental investigations of a number of operating parameters were performed to assess their effect on the removal of Cu (II) by AC from synthetic solutions. These parameters are contact time, adsorbent dose, initial concentration of adsorbate, agitation rate, solution temperature and pH level. After equilibrium was attained, the metal uptake capacity for each sample was calculated according to a mass balance on the metal ion using equation (1) (H.G. Ibrahim, et al., 2009).

$$q_e = \frac{V\,(C_o - C_e)}{W} \qquad 1$$

Where W is the mass of adsorbent (g), V is the volume of the solution (L), C_o is the initial concentration of metal (*mg* L^{-1}), C_e is the equilibrium metal concentration (*mg* L^{-1}) and q_e is the metal quantity adsorbed at equilibrium (*mg/g*).

The percent removal of Copper from the solution was calculated by the following equation (2) (H.G. Ibrahim, et al., 2009).

$$R\% = \frac{(C_o - C)}{C_o} \times 100 \qquad 2$$

Where C_o (mg/L) is the initial metal ion concentration and C (mg/L) is the final metal ion concentration in the solution and R is the removal percentage (%).

Selection of the Wavelength

Figure (1) shows the maximum absorbance of Cu (II) solutions. The wavelength was selected so that it is located in an area that represents the highest absorption, the optimum wavelength is λ_{max} = 615 nm.

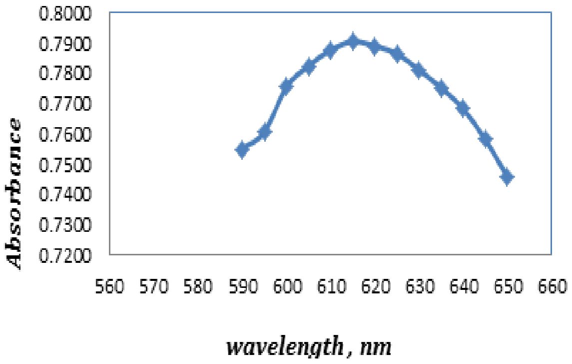

Figure 1 Maximum Absorbance of Cu (II) solutions

Calibration Curve

By following the optimum conditions given under standard method of analysis in constructing calibration curves, Beer's relationship for *Cu (II)* solutions. The reproducibility of the method was tested by known concentration of *Cu (II)* solutions. (25, 50, 75, 100 and 150 ppm). The calibration curve for *Cu (II)* ions represents values measured by *Spectrophotometer* plotted against the concentration of *Cu(II)* in figure (2).

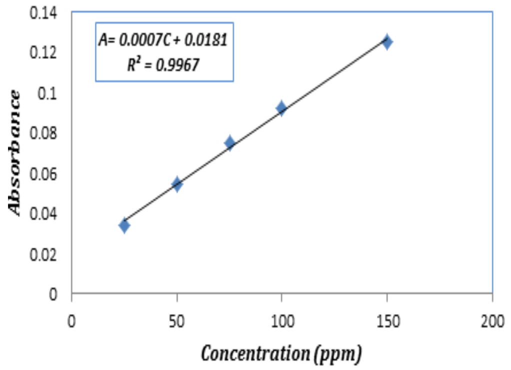

Figure 2 Beer's relationship for Cu (II) ions

Parameters Effects on Adsorption of Copper

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.

Effect of Contact Time Variation

The effect of contact time on the removal efficiency and adsorption capacity of *Cu (II)* ions was investigated, the contact time studied was ranged from 0 to 120 *min* (15, 30, 60, 90 and 120 min). The removal percentage of *Cu (II)* from the tanning solutions is investigated for 100 *ml* containing known concentration of *Cu (II)* solutions (25, 50, 75, 100 and 150 *ppm*) at agitation rate 200 rpm, adsorbent dose 1 *g*, particle size (0.375 < d < 0.5) mm, pH value 5 and temperature at 35 °*C*.

Results in figure (3) show that, the removal percentage of *Cu (II)* from wastewater increases as the contact time increases until the equilibrium had been reached. Where the equilibrium was started to reach after 90 *min*

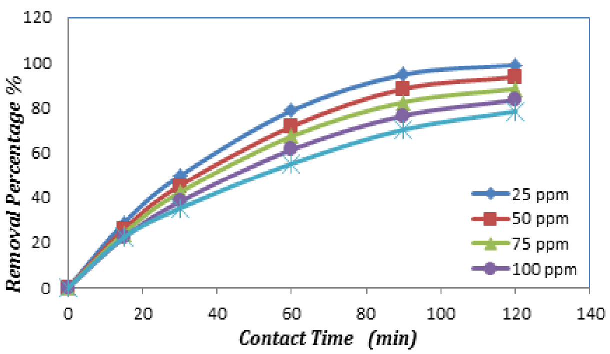

Figure 3 Effect of contact time variation on removal percentage of *Cu (II)*

This increment may be attributed to the increase in agitation time which results in decreasing in the adsorption sites on adsorbents which were gradually filled up by metal ions and the kinetics become dependent on the metal ions were transported from the bulk liquid phase to the actual adsorption sites. (Orumwense, F, 1996).

Effect of Adsorbent Dose Variation

The effect of the amount of adsorbents on adsorption of *Cu (II)* was examined under constant conditions of contact time of 120 *min* at 200 *rpm*, for 100 *ml* containing known concentration of *Cu (II)* solutions (25, 50, 75, 100 and 150 *ppm*), pH at 5, temperature at 35 ^{o}C and the particle size is (0.375 < d < 0.5) *mm*, where the mass of adsorbent was 0.5, 1 and 2 g.

The results shown in the figure (4) indicate that the removal percentage of *Cu (II)* increases with increasing the adsorbent dose. This is due to increasing the surface area of *AC* and hence more active sites are available for the adsorption of more *Cu (II)* ions. It is also evident from the figure that an adsorbent dose of 1 *g* per 100 *ml* of tanning solution corresponds to a complete removal of *Cu (II)* from the solution at small concentration (25 and 50 *ppm*) under the operating conditions, while the completely removal of *Cu (II)* for the concentrations 75, 100 and 150 *ppm* were occurred with 2 *g*.

Generally, a dose of 1 *g* of *AC* per 100 *ml* of solution results in a relatively high percent removal of 98.86, 93.37, 88.17, 83.24 and 78.26 for the concentration 25, 50, 75, 100 and 150 ppm respectively.

Larger amount of *AC* exceeding those in the synthetic solutions as the case with the tannery wastewater concentration require larger amount of *AC* to provide a larger surface area to allow the adsorption process to proceed. The results reveal that the optimum adsorbent dose is 1 *g*.

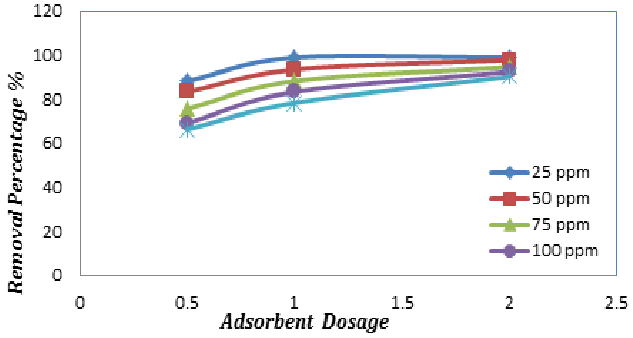

Figure 4 Effect of Adsorbent Dose variation on removal percentage of *Cu (II)*

Effect of Initial Concentration Variation

The effect of initial *Cu (II)* ion concentrations on the adsorption efficiency of *AC* is shown in figure (5). Adsorption experiments were carried out at different initial *Cu (II)* concentrations ranging from 25 to 150 *mg/l* (25, 50,75,100 and 150) for 120 *min* at 200 *rpm* with 1 *g*/100 ml of solution were used, solutions pH at 5, and temperature at 35 ^{o}C and the particle size is (0.375 < d < 0.5) *mm*.

From figure (5) It was observed as a general trend that there was decreasing in the removal percentage with increasing of the initial concentration. This increase is a result of increase in the driving force (i.e. gradient of concentration). However, the decrease in percentage removal may be explained on the basis that the increase in the number of ions competing for the available binding sites and also because of the lack of active sites on the adsorbent at higher concentrations. Therefore, more metal ions were left un-adsorbed in solution at higher concentration levels (Oljira, L. 2016).

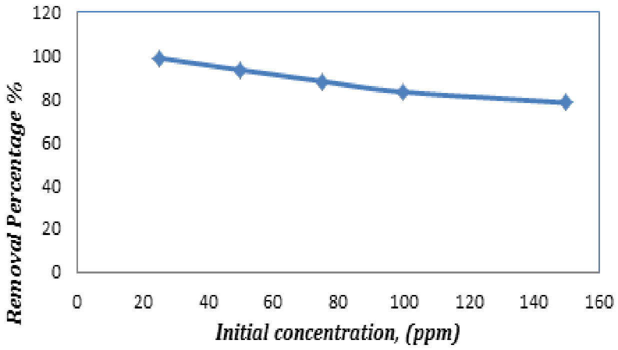

Figure 5 Effect of Initial Concentration on removal percentage of *Cu (II)*

At lower initial *Cu (II)* concentrations the ratio of surface active sites to the total *Cu (II)* ions in the solution is high and hence all *Cu (II)* ions may interact with the adsorbent and be removed from the solution. However, the amount of *Cu (II)* adsorbed per weight unit of adsorbent (adsorption capacity) is higher at high concentrations (Oljira, L. 2016).

At lower initial *Cu (II)* concentrations, sufficient adsorption sites are available for adsorption of *Cu (II)* ion. Therefore, the fractional adsorption is independent of the initial *Cu (II)* ion concentration. However, at higher concentrations the numbers of *Cu (II)* ions are relatively higher compared to availability of adsorption sites (Oljira, L. 2016).

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, 200, 300 and 500 *rpm* using 1 *g* of *AC* of particle size (0.375 < d < 0.5) *mm* at temperature 35 *°C*, initial pH of 5 and 120 minutes of contact time.

Results in figure (6) show that, the removal percentage of *Cu (II)* from wastewater increases as the agitation rate increases. The removal percentage of *Cu (II)* increases from 85.18% to 99.54%, 79.03 to 96.07%, 70.18 to 93.12%, 62.04 to 89.19% and 58.25 to 85.44%, for an initial concentration of 25, 50, 75, 100 and 150 *ppm*, respectively as the agitation rate increases from 100 to 500 *rpm*.

The results reveal that the optimum agitation rate is 200 *rpm*, corresponding to removal efficiencies 98.86, 93.37,88.17,83.24 and 78.27 % for an initial concentration of 25, 50, 75, 100 and 150 *ppm*, respectively.

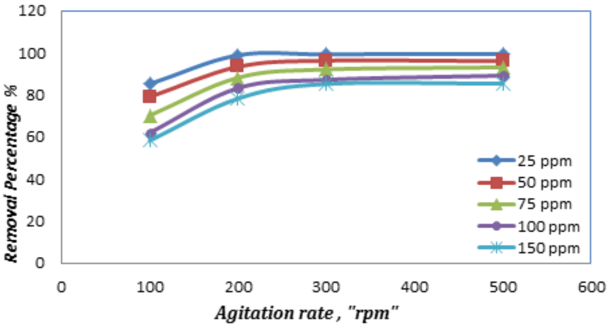

Figure 6 Effect of agitation rate variation on removal percentage of *Cu (II)*

Effect of Temperature

Temperature effect on the adsorption of *Cu (II)* from 100 *ml* of solutions containing known concentration of *Cu (II)* solutions (25, 50,75,100 and 150 *ppm*) are investigated using 200 *rpm* agitation rate, 1 *g* of *AC* of (0.375 < d < 0.5) *mm* particle size, an initial pH equal to 5 and contact time 120 min at 35, 45, 55 and 65 *°C*.

The results in figure (7) show that the removal percentage increases as temperature increases as an indication that the process in endothermic in nature.

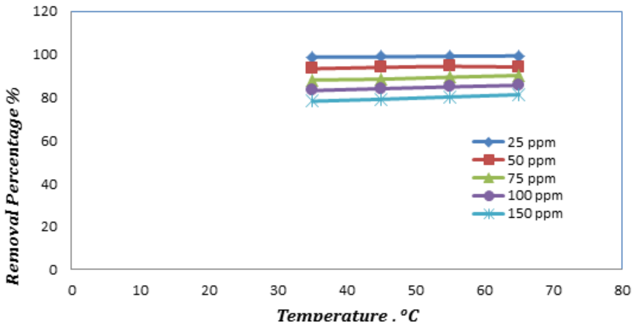

Figure 7 Effect of temperature variation on removal percentage of *Cu (II)*

An increase in the temperature of the solution causes the kinetic energy of the adsorbate particles to increase so the velocity of the adsorbate molecules. The optimum temperature was found to be 35 ^{0}C.

Effect of pH

The pH of solution is considered one of the major factors effecting the adsorption process using *AC*. 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 90 *min* at 200 *rpm* for 100 *ml* of 75 *ppm* of *Cu (II)* solution, 1*g* of *AC* of (0.375 < d < 0.5) *mm* particle size and temperature at 35 *°C* and the solution pH from 3 to 7 (3, 4, 5, 6 and 7).

Figure (8) depicts the effect of pH on removal% of copper (II). It was found that adsorption of Cu (II) ion from the solution was strongly pH dependent. At pH 3-3.9 range the adsorption was low and rapidly increased between pH 4-5 resulting greater removal efficiency. It was found that adsorption of Cu (II) ion from the solution was strongly pH dependent. This phenomenon can be explained by the presence of H^+ ion in the solution at lower pH. At pH less than 4, hydrogen protons may compete with metal ions for active binding sites on the surface of Pine Activated Carbon, which leads to fewer binding sites being available to bind metal ions, so the adsorption amount of Cu (II) was very little. As the pH increases, the adsorption surface became less positive and therefore electrostatic attraction between metal ions and the surface of Pine Activated Carbon was increased resulting greater removal efficiency between pH 4-5. The result depicts that removal% was increased steadily up to pH 5, attains maximum value of about 98.86%. However, after pH 5, there is decrease in adsorption.

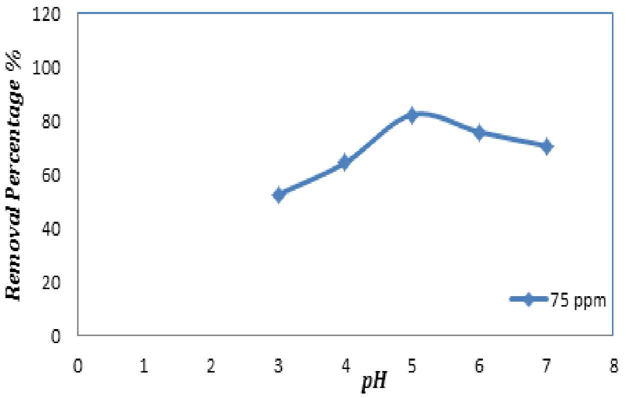

Figure 8 Effect of pH variation on removal percentage of *Cu (II)*

Adsorption Kinetics

The kinetics of adsorption was studied for 100 *ml* containing known concentration of *Cu (II)* solutions 75 *ppm* at contact time ranging 15-90 min (15, 30, 60 and 90). The experimental data was fitted to the pseudo first order and pseudo second order kinetic model by using equations (3) and (4) in Figure (9) and Figure (10), respectively.

$$\ln(q_e - q_t) = -k_1 t + \ln(q_e) \qquad 3$$

$$\frac{t}{q_t} = \frac{1}{k_2 * q_e^2} + \frac{t}{q_e} \qquad 4$$

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

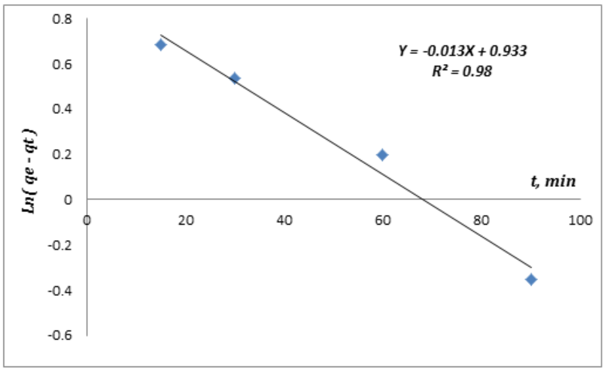

Figure 9 Pseudo first order kinetics plot for *Cu (II)* adsorption

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. Heavy metal adsorption is usually modelled by the classical adsorption isotherms Langmuir and Freundlich isotherms models. In order to study the adsorption isotherm of Cu (II) on studied adsorbent, the experimental adsorption data that observed under same conditions of effect of initial concentration was fitted to Langmuir and Freundlich models. Figures (11) and (12) show the plots of Langmuir model and Freundlich model using Eqs (5) and (6).(H.G. Ibrahim, et al., 2009) respectively for removal of copper.

$$\frac{C_e}{q_e} = \frac{1}{q_m k_l} + \frac{C_e}{q_m} \qquad 5$$

$$\ln(q_e) = lmk_F + \frac{1}{n} lnC_e \qquad 6$$

The values of various constants of the models were calculated and represented in the Table (1).

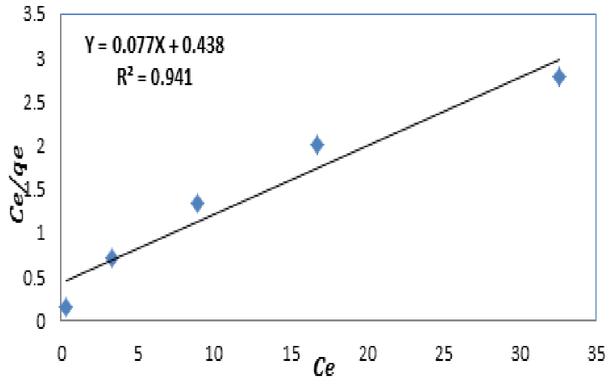

Figure 11 Langmuir adsorption isotherm for *Cu (II)* adsorption

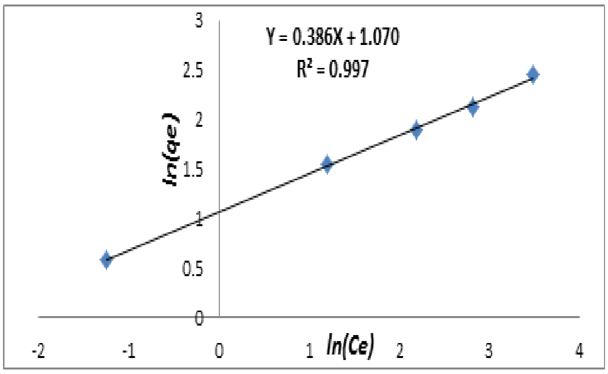

Figure 12 Freundlich adsorption isotherm for *Cu (II)* adsorption

Table 1 Isotherm constants for Cu (II) adsorption

Isotherms	Values
Langmuir	
q_m (mg/g)	12.98701
K_L (L/mg)	0.175799
R^2	0.941
Freundlich	
K_F (mg/Kg)	2.915379
N	2.590674
R^2	0.997

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.

CONCLUSION

The adsorption was influenced by various parameters including: temperature, initial concentration, different size of activated carbon (*AC*), dose of adsorbent, contact time, pH and agitation rate. The Langmuir and Freundlich adsorption isotherm models were used for the description of the adsorption equilibrium and Kinetic studies of adsorption was studied.

Based on the results of this study, following conclusions could be drawn:

- The contact time has significant impact on the adsorption removal of copper where the removal was fast in beginning and then decreases until the equilibrium is starting to reach 90 *min*.
- The adsorption removal efficiency also affected by the amount of adsorbent added to the solution. As the amount of adsorbent increases, the removal efficiency increases. The results reveal that the optimum adsorbent dose is 1 *g*.
- The initial metal ion concentration affects the adsorption removal efficiency. The removal efficiency decreases with an increasing in the initial metal ion concentration of *Cu (II)*.
- The adsorption removal efficiency also affected by temperature. The removal percentage increases as temperature increases. the optimum temperature was found to be 65^0C.
- The pH plays important role in removal of copper from wastewater. The variation in the amount of adsorption clearly indicated the influence of pH on adsorption process, increase of pH from 3-5 range leading to increases to the amount of copper removal percentage. The optimum pH of solution for *Cu (II)* removal was found to be 5.
- The effect of agitation rate on *Cu (II)* removal 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 200 *rpm*.
- Kinetic studies of adsorption revealed that the adsorption process followed a pseudo second order kinetic model for the adsorption of copper.
- The adsorption data were fitted to two isotherm model equations, and the Freundlich model was found to be the best model for the adsorption of copper.

REFERENCES

Aydın, H., Bulut, Y., Yerlikaya, Ç., (2008). Removal of copper(II) from aqueous solution by adsorption onto low-cost adsorbents. J. Environ. Manag. 87, 37e45.

Chuah, T.G. Jumasiah,A. Azni,I. Katayon, S and Thomas Choong, S.Y. (2005), Rice husk as apotentially low-cost biosorbent for heavy metal and dye removal: an overview, Desalination, 175(3), 305-316.

Demirbas¸, E., Dizge, N., Sulak, M.T., Kobya, M.(2009). Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon. Chem. Eng. J. 148, 480e487.

Feng, N., Guo, X., Liang, S., (2009). Adsorption study of copper(II) by chemically modified orange peel. J. Hazard. Mater. 164, 1286e1292.

Ho,Y.S. (2003). Removal of copper ions from aqueous solution by tree fern, Water Res37, 2323-2330.

Ibrahim,H.G. (2010).Removal and Recovery of Chromium from Aqueous solutions, LAP LAMBERT Academic Publishing GmbH & Co. KG, Germany, Ibrahim,H.G. Okasha,A.Y. Aboabboud, M.M. and Awad,A.N. (2009). Removal of Copper From Aqueous Solutions by Adsorption Technique onto Low Cost Material, The 3rd National Conference of Basic Science, Gharian, Libya, 25-27th April, No. CH12

Issabayeva,G. and Aroua,M.K. (2011).Removal of copper and zinc ions onto biomodified palm shell activated carbon, World Acad. Sci. Eng. Technol.,76, 259-262.

Kadirvelu K, Thamaraiselvi K, and Namasivayam, (2001). Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste, Bioresour Technol. Jan;76(1):63-5.

Li, K., Zheng, Z., Li, Y., (2010). Characterization and lead adsorption properties of activated carbons prepared from cotton stalk by one step H3PO4 activation. J. Hazard. Mater. 181, 440e447.

Milenković, D.D. M.M. Milosavljević, A.D. Marinković, V.R. Đokić, J.Z. Mitrović, and A.L. Bojić, Removal of copper(II) ion from aqueous solution by high-porosity activated carbon, Water SA, 39(4), 2013, 515-522.

Oljira, L. (2016).Adsorption of heavy metals from constituent wastewater by tea waste adsorbent . Addis Ababa, Ethiopia, June.

Orumwense, F (1996). Removal of lead from water by adsorption on a kaolinitic clay. J. Chem. Technol. Biotech,

Wan, M.W., Kan, C.C., Rogel, B.D., Dalida, M.L.P., (2010). Adsorption of copper(II) and lead (II) ions from aqueous solution on chitosan-coated sand. Carbohydr. Polym. 80, 891e899.