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Adsorption of Copper Ions from Aqueous Solution Using Raw and Modified Can Papyrus: Experimental and Kinetic Study

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Abstract

The adsorptions of copper ions from aqueous solution by can papyrus were studied using batch and continuous adsorption. It has been improved surface area and efficiency of the cane papyrus using urea and thiurea at different concentrations through stirring in period of time with mixer. Results proved that cane papyrus very well in the adsorption of metal through the study of important variables and influences such as the contact time, pH in addition to the initial concentration. It was found that the effect of pH at 6 to 7 better than acid or base solution also found that the best time for adsorption to reach equilibrium is 90min and there is no effect of temperature significantly on the results observed, studied the effect of weight of the cane where found that 0.4g best weight. After treatment with urea and thiurea the results improved from the 56% removal by natural cane, 61% for urea modified and 68% for thiurea modified. For continuous adsorption the results shows that when the flow rate increase in constant bed of adsorbent the breakthrough decrease. As well as the best curve was obtained using a cane modified with thiurea weighing 2.5g in a continuous flow rate where the breakthrough curve is start from 25min to 175min. The results was applied to Langmuir and Freundlich adsorption isotherms, the results fitted will to both at correlation coefficients 0.971 and 0.9066 for Langmiur and Freundlich respectively. Pseudo second order was applied and gives better results for adsorption where R^2 is 0.9941 while for pseudo first order R^2 is 0.136.

Keywords: *Adsorption, Canpapyrus, Cupper*

1 Introduction

The presence of heavy metals in the environment is a major concern due to their toxicity for many life forms. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metals will not degrade into harmless end products and accumulate in living organisms, causing various diseases and disorders [1, 2].

Heavy metals contaminant exist in wastewater of many industrials, such as refinery, metal plating facilities, mining operations and many other industrials, its well-known that some metals are harmful to life such as chromium, cadmium, lead, copper mercury, zinc, etc. they are significantly toxic to human beings and ecological environments [3].

Researchers worldwide have developed a number of methods such as chemical precipitation, oxidation or reduction, ion exchange, filtration, membrane separations, electrochemical treatment, reverse osmosis, evaporation recovery, coagulation and etc., for removing the toxic metals from industrial effluents before discharging into aquatic streams [4].

The conventional treatments produce toxic chemical sludge and in turn disposal or treatment becomes costly and not ecofriendly. Adsorption is considered as one of the effective and economical technology compared to others for removal of toxic metals from effluents. Activated carbon is widely used in many industries as an effective adsorbent for toxic metal removal.

The cost of activated carbon is high that usually industries strive for low cost methods for waste water treatment and hence may option for low cost adsorbents. Though researches reported shows varieties of low cost adsorbents, all adsorbents are not available easily throughout the world. Hence, considering the availability of materials in particular region, the adsorbents may be suitably selected to cater the needs of that region [5].

In this work can papyrus had been used which it took from collage of Political Science- Baghdad university as natural adsorbent to remove Cu(II) ions from its aqueous solution and search the efficiencies of using it as low cost adsorbent.

The point of the study is can papyrus treated with urea and thiurea to modified active site in order to increase the removal efficiency of the metals by adsorption.

2 Materials and Methods

2.1 Preparation and Modification of Can Papyrus

The papyrus used in this study was collected from Baghdad University College of political science's river where it grows naturally and easily found. There were several steps before using the can papyrus in our experiments. Staring with cleaning with distilled water many times, drying it for 4hr at 110°C, then crashed it to smaller parts after that washing again with distilled water, then drying again at 110°C for 4hr, then the dried cans was crashed using coffee machine. The cans sieved in mesh to remove the undesired parts. Then finally wash it several times with distilled water to remove all dust and soil, and dried it again and then stored in container to use it. 5 g from raw can papyrus (R-CP) was mixed in a beaker with 100 ml of (0.5, 0.1, 0.15, and 0.2M) urea and thiurea solutions, and allowed to soak for 24 hrs, then the mixture was filtered to remove the adsorbent, which was washed several times with distilled water to provide natural pH. The adsorbents were then oven-dried at 100 C for 4 hrs.

2.2 Solution preparation

A standard stock solution of Cu(II) 500 ppm was prepared by adding 4.3 g of Copper(II) Sulfate Pentahydrate in 1000 ml distilled water in volumetric flask, It was dissolved by magnetic stirrer for 1 hr.

2.3 Batch adsorption studies

Batch process experiments were conducted in a shaker to get good mixing in addition to get more than one experiment in one time; the volume of Cu(II) solution used in this study is constant 50ml for all samples, and the solution was filtered using filter papers. In this study, the contact time was varied from 15 to 220 min, the pH of the solution from 2 to 8, the initial concentration from 5 to 40 ppm, and the amount of adsorbent from 0.1 to 1.1 g. A Perkin-Elmer model 5000 atomic absorption spectrometer (AAS) was used for copper analysis. The results are expressed in terms of removal percentage (%) of Cu (II) ion and adsorption capacity (mg/g) of the raw and modified can papyrus, according the following relationships:

$$q_t = \frac{V(Co - C)}{m} \quad \ldots\ldots(1)$$

$$\%\text{Removal} = R = \frac{Co - C}{Co} * 100 \quad \ldots(2)$$

Where, C_0 and C are the initial and final Cu (II) concentrations (ppm) respectively, V the volume of Cu solution (L) and m the weight of adsorbent (g).

2.4 Continuous Adsorption Studies

The continuous adsorption studies were conducted in a glass column with 2.5 cm in-diameter and 20 cm deep operated with dozing pump in a gravity down-flow mode. First, 500 mL of distilled water was passed through the packed column to make the packing more compact. Stock solutions of Cu (II) were allowed to flow in through dozing pump to the packed column. The parameters varied in the continuous experiments were weight of adsorbent (bed-height), inlet Cu (II) concentration, flow rate speed, and modified adsorbent. The continuous experiments were carried out at neutral pH value (6-7) obtained by batch experiments.

Samples were collected from the exit of the column at different time intervals and analyzed for Cu (II) ions using AAS. Operation of the column was stopped when the effect of the adsorbent on Cu (II) ion concentration reach its limit. The first Sample collected at the first 5 minute and the rest collected every 15 minute and that apply for all the continuous sets.

3 Results and Discussion

3.1 Batch Experiments

3.1.1 Effect of pH

The pH of solution has been identified as the most important variable administrates the metal adsorption. The percentage removal of copper by can papyrus increased as the pH of the solution increased and reached a maximum value at pH 8 as shown in figure 1. Cu(II) precipitate as Cu $(OH)_2$ at pH value of 4-6[6]. Actually the insoluble precipitation of Cu $(OH)_2$ would occur at pH value above 4-5 [7]. It can be observed optimal pH values around 6 - 7. The increase in metal removal with increase in pH values can be explained on the basis of a decrease in competition between proton and the metal cations for the same functional groups and by the decrease in positive charge of the adsorbent which results in a lower electrostatic repulsion between the metal cations and the surface [7].

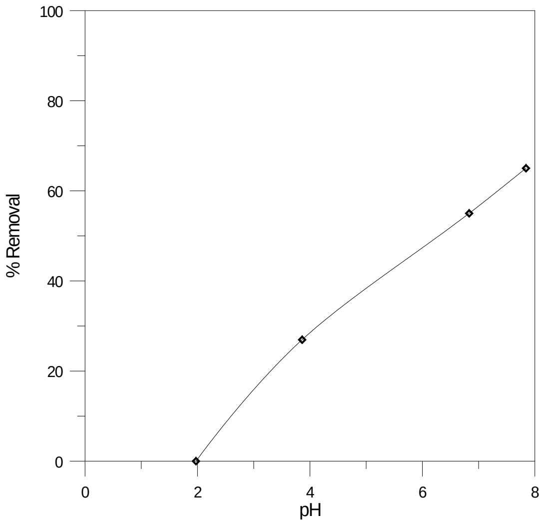

Figure 1: Effect of the pH on the adsorption removal of Cu(II) over 0.5g raw papyrus for 10ppm and 15min

3.1.2 Effect of Contact Time

The effect of contact time was studied for an initial Cu(II) concentration of 10ppm, pH is 7 and adsorbent weight is 0.5g. The figure 2 shows a rapid initial adsorption rate of Cu(II) at the beginning until 90 min of contact time, thereafter, the adsorption rate became practically constant. The variation in the extent of adsorption may be due to the fact that initially all sites on the adsorbent surface were vacant and the solute concentration gradient was relatively high [6].

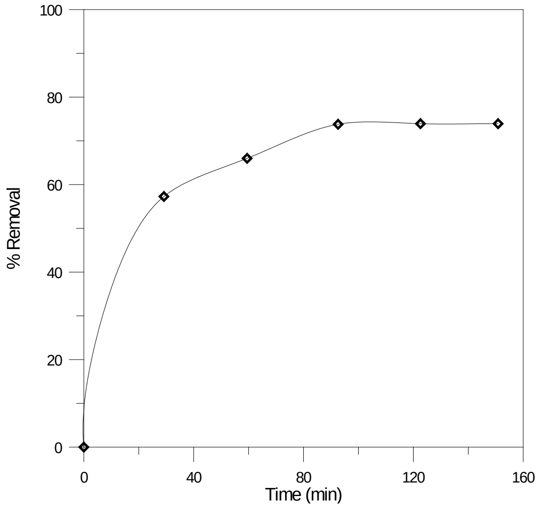

Figure 2: Effect of Contact Time on The Adsorption Removal of Cu (II) at pH 7 and 10ppm of solution

3.1.3 Effect of Initial Concentration

The adsorption of Cu(II) on papyrus was highly depend on initial metal concentration, when the initial concentration of Cu(II) increase from 5 to 40 ppm, the percentage removal of Cu(II) ions decrease rapidly from 58% to 26% as shown in figure 3. These results show that the percentage of removal decreases with increasing initial Cu(II) concentration. This can be explained that all the natural adsorbent has a limited number of active sites, which become saturated at a certain concentration.

3.1.4 Effect of Temperature

The effect of temperature on the adsorption removal of Cu (II) was studied at temperature interval of 25, 35, 45, and 55 ^{o}C with the other parameter are constant. As shown in figure 4 increasing the temperature would give a reverse effect so the 45 ^{o}C would be the perfect temperature for removing the copper but the efficiency is not big difference from 25^{o}C.

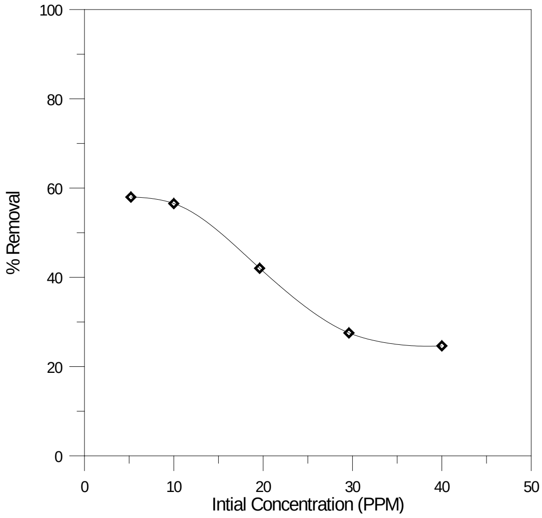

Figure 3: Effect of The initial concentration on The Adsorption Removal of Cu (II) for pH 7 and 0.5g of papyrus

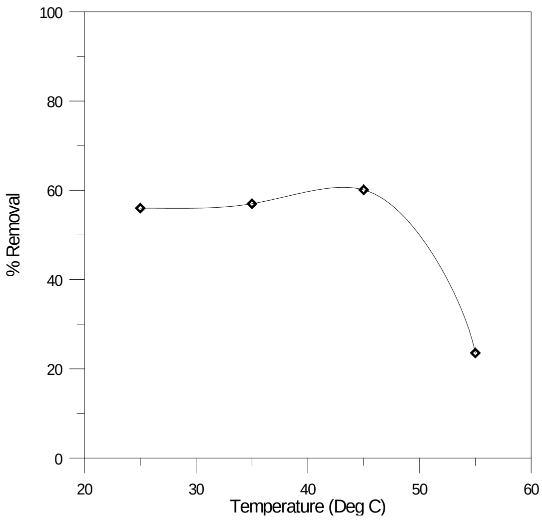

Figure 4: Effect of The temperature on The Adsorption Removal of Cu (II) in the constant conditions

3.1.5 Effect of Papyrus Dose

The effect of the can papyrus dose on the adsorption removal of copper ions was studied at different weight while keeping the other parameters constant. Figure 5 shows that removal increased with increase in adsorbent dosage until 0.4g due to the greater availability of the exchangeable sites or surface area, this can be explained as adsorbent dose increased, more and more surface area will be available which exposed more active sites for binding of metal ions. For a given initial concentration of Cu(II), further increase of the adsorbent mass don't have practically any effect on the adsorption rate of cupper.

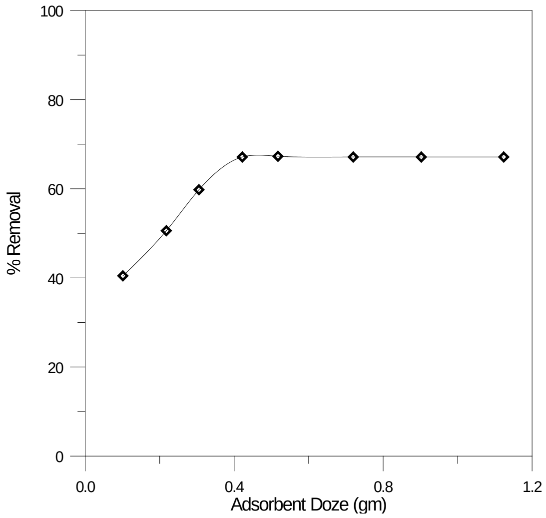

Figure 5: Effect of papyrus dose on the adsorption removal of Cu (II) at pH 7 and initial concentration 10ppm

3.1.6 Effect of the can papyrus modifications

In order to have a better comparison, the adsorptive removal of Cu(II) ions by modified can papyrus was compared with that of raw can papyrus. Comparing the results, it appears that the maximum adsorptive removal percent of Cu(II) ions using can papyrus modified with urea and thiurea was higher than raw can papyrus as shown in figure 6, as for example at 0.4g of adsorbent the removal was increased from 56% to 61% for modified urea and 68% for modified thiurea These findings may be referring to the nature of urea and thiurea that provided more binding sites within each of their substrates for copper ions. Based on the obtained data we conclude that either urea or thiurea can be used to enhance the removal of heavy metals from aqueous solutions using can papyrus.

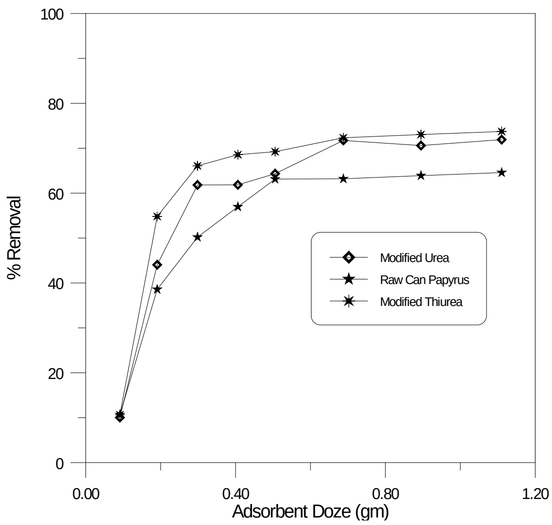

Figure 6: Comparison between raw and modified can papyrus

3.2 Continuous Experiments

3.2.1 Effect of initial Cu Concentration

The effect of the initial copper concentration on the adsorption process with 10, 20, and 30 ppm at constant flow rate, and fixed papyrus weight 0.4g of thiurea modified was shown in figure 7. The increase in the copper concentration makes the break through curve much sleeper; this would be expected on the basis that the driving force for mass transfer increases with increase of concentration of adsorbate in the solution [8]. A high adsorbate concentration may saturate the adsorbent more quickly, thereby decreasing the breakthrough time. The same conclusion was obtained by [9, 10].

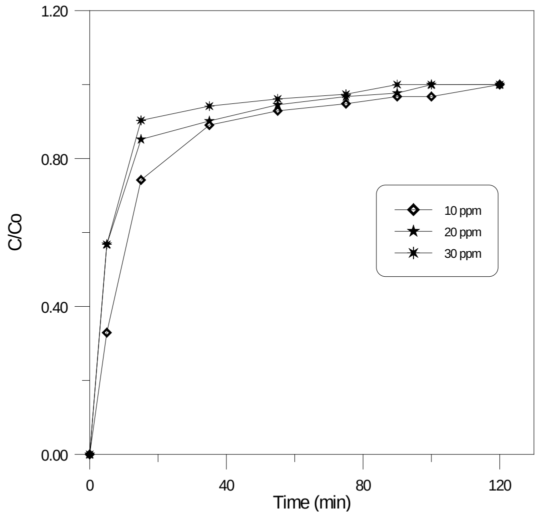

Figure 7: Effect of copper initial concentration on breakthrough curve at pH7 and 0.4g of modified papyrus

3.2.2 Effect of Can Papyrus Dose (bed depth)

The adsorption of copper in the packed bed column is largely dependent on the quantity of can papyrus backing. The effect of can papyrus weight was studied at concentration 10 ppm, flow rate 20ml/min and 25 C. Figure 8 shows that when the can papyrus weight decreased it reach the breakthrough time faster than for low quantity, as for example for 1.5g and 2g of papyrus need 25 to 75min to reach breakthrough while for 2.5g reach it from 25 to 175min means long breakthrough.

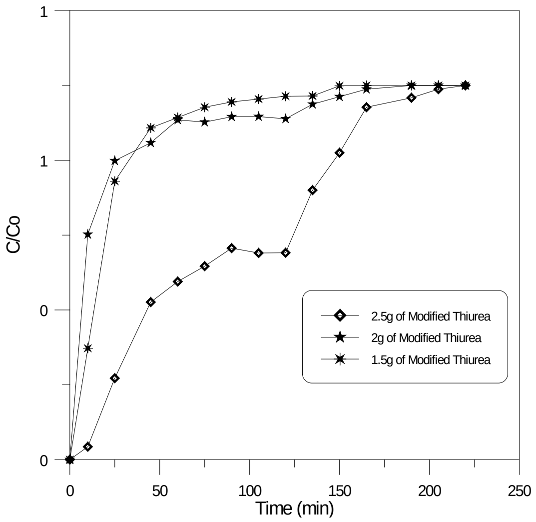

Figure 8: Effect of can papyrus weight on the breakthrough curve

3.2.3 Effect of Flow Rate

The effect of flow rate on adsorption was studied at different flow rate 20, 30 and 40 ml/min, constant concentration 10ppm and weight of modified papyrus is 0.4g. The results showed an increase in the adsorbate flow rate decreases the breakthrough time due to the decrease in the contact time between the adsorbate and the adsorbent along the adsorption bed. Increasing the flow rate may be expected to make reduction of the surface film. Therefore, this will decrease the resistance to mass transfer and increase the mass transfer rate and there is not enough time for adsorption equilibrium to be reached which results in low bed utilization and the adsorbate solution leaves the column before equilibrium. These results agree with that obtained by [9, 10 and11]. From figure 9 it is observed that at higher flow rate, the rate of reaching the breakthrough time is faster where as in lower flow rate the rate of reaching the breakthrough time is slower. This is due to the residence time distribution of influent concentration to the adsorbent is greater in lower flow rate [12, 13].

3.3 Adsorption Isotherms

Adsorption isotherms show the distribution of solute between the liquid and solid phases and can be described by several mathematical relationships such as the standard Langmuir and Freundlich models were as shown in the Figures 10 and 11. The linearized Langmuir and Freundlich adsorption isotherms obtained are shown in the Table 1 with the values of linear regression coefficients.

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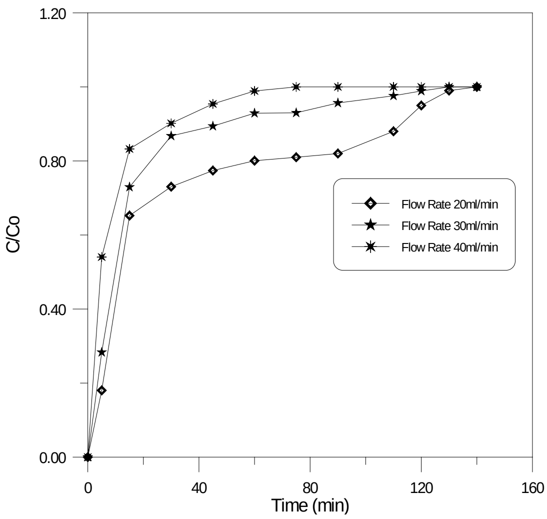

Figure 9: Effect of flow rate on the breakthrough curve

Table 1: Isotherm parameters for the adsorption of Cu onto can papyrus at different initial conditions

Langmuir	K_L	α_L	R^2
	4.955	0.169	0.971
Freundlich	K_f	n	
	0.029	0.471	0.906

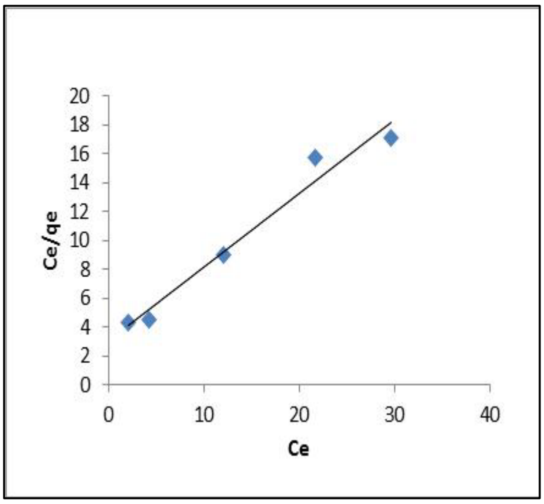

Figure 10: Langmuir Isotherm for adsorption of Cu ions at different concentration

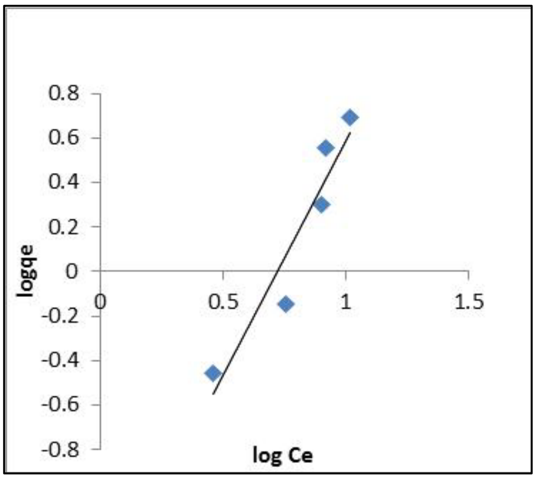

Figure 11: Freundlich Isotherm for adsorption of Cu at different concentration.

3.4 Adsorption Kinetics

In order to define the adsorption kinetics of heavy metals ions, the kinetic parameters for the adsorption processes were studied for the contact times ranging between 1 to 150 min pseudo first order, and pseudo second order models were applied to experimental data as shown in Figures12 and 13.The comparison of experimental sorption capacities (qt) and the predicted values (qe, k_1, k_2, R_2) from pseudo first order, and pseudo second order constants are given in Table 2 The pseudo first order was not satisfactory to explain the experimental data , whereas the calculated, qe values derived from the pseudo second order model for sorption of metal ions were very close to the experimental (qe) values. The second order equation appeared to be the better fitting model than first order because it has higher R_2 value.

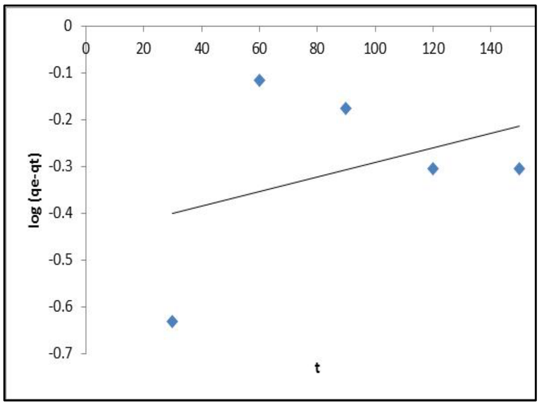

Figure 11: Pseudo first order model for copper.

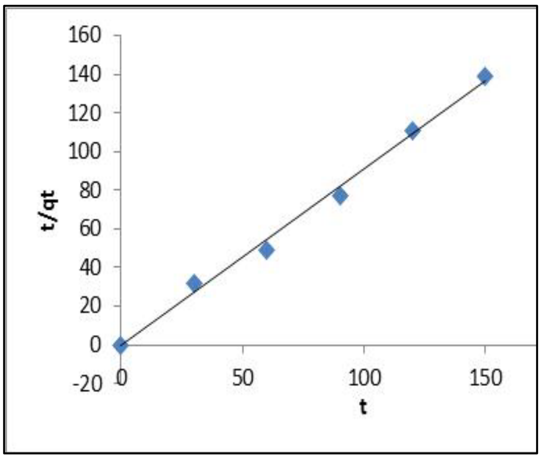

Figure 12: Pseudo second order model for copper.

Table 2: Kinetic parameters of copper sorption by can papyrus at different time interval

Pseudo 1st order kinetic model	K_1	q_e	R^2
	0.00368	0.3577	0.1369
Pseudo 2nd order kinetic model	K_2	q_e	R^2
	1.323	1.09	0.9941

4 Conclusions

Batch studies on copper removal showed significant effects of the variables adsorbent dose, contact time, initial metal concentration, pH, and temperature. The results provide a good indication of the different operating conditions that would be required for efficient removal of cupper from aqueous solution. The modification increased the percentage removal because of the increasing in the active sits. Adsorption isotherms also give good fitting to experimental data in addition the pseudo second order is fitted will than pseudo first order models.

5. Reference

[1] Bailey, S. E., Olin, T. J., Bricka R. M. and Adrian, D. D., (1999) A review of potentially low-cost sorbents for heavy metals‖, Water Research, 33, 2469-2479

[2] Cheung, C. W., Porter J. F. and McKay, G.,‖ (2001) Sorption kinetic analysis for the removal of cadmium ions from effluents using bone char‖, Water Research, 35, 605-621.

[3] Dorris K L, Zhang Y, Shukla A et al. (2000) The removal of heavy metal from aqueous solution by sawdust adsorption removal of copper‖,hazared mater, b80;33-42.

[4] Patil Kishor P, Patil Vilas S, Nilesh Patil, Motiraya Vijay, (2012) Adsorption of Copper (cu 2+) & Copper (zn2+) Metal

Ion from Wastewater by Using Soybean Hulls and Sugarcane Bagasse as Adsorbent‖, International Journal of Scientific Research and Reviews, Vol. 1(2), pg 13-23.

[5] Mukesh Parmar and Lokendra Singh Thakur, (2013) Heavy Metal Cu, Ni and Zn: Toxicity, Health Hazards and their removal techniques by Low Cost Adsorbents: A Short Overview‖, International Journal of Plant, Animal and Environmental Sciences,Vol. 3, pg 143-157.

[6] Wang, X.S., Qin, Y.,. (2005) Equilibrium sorption isotherms of Cu2+ on rice bran. Process biochemistry.

[7] Aksu, Z.,Isoglu, I.A.,. (2005) Removal of copper (II) ions from aqueous solution by bio sorption onto agricultural waste sugar beet pulp. Process biochemistry.

[8] Malkoc, E. and Nuhoglu, Y., (2006) Fixed bed studies for the sorption of chromium (VI) onto tea factory waste. Chemical Engineering Science, , 61, 4363-4372.

[9] Lin, S. H. and Wang, C. S., (2002) Treatment of high-strength phenolic wastewater by a new two-step method, Journal of Hazardous Materials, B90, pp 205-216.

[10] Sulaymon, A. H., and Ahmed, K. W., (2007) Competitive adsorption of furfural and phenolic compounds onto activated carbon in fixed bed column, Environ. Sci. Technol.

[11] Gupta, A., Nanoti, O. and Goswami, A. N., (2001) The removal of furfural from water by adsorption with polymeric resin, Separation Science and Technology, 36, 13, 2835-2844.

[12] Sugashini S. and Meera Sheriffa K. M., (2012) Optimization using central composite design (CCD) for the biosorption of Cr (VI) ions by cross linked chitosan carbonized rice husk (CCACR),‖ Clean Technologies and Environmental Policy.

[13] Han R., Wang Y., Yu W., Zou, Shi, and Liu, (2007) Biosorption of methylene blue from aqueous solution by rice husk in a fixed bed Column‖ Journal of Hazardous Materials, 141, 3,713–718.

أمتزاز ايون النحاس من المحلول المائي باستخدام قصب البردي الخام والمطور: دراسة عملية ونظرية

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الخلاصة

تم دراسة امتزاز أيون النحاس من المحاليل المائية باستخدام طريقة الامتزاز الساكن والمستمر بوجود عامل ماز طبيعي هو قصب البردي. تم تحسين المساحة السطحية والكفاءة لقصب البردي باستخدام مادة اليوريا والثايوريا بتراكيز مختلفة من خلال نقعها لمدة زمنية محددة مع الخلط. اثبتت النتائج ان قصب البردي جيد جدا في امتزاز المعادن وذلك من خلال دراسة المتغيرات والتأثيرات المهمة مثل الوقت والاس الهايدروجيني بالاضافة الى التركيز الاولى للنحاس في محلولهه الماءي. حيث وجد ان تاثير الاس الهايدروجيني عند 6 الى 7 افضل من الحامضي او القاعدي كما وجد ان افضل وقت للامتزاز للوصول الى الاستقرار هو 90دقيقة كما ولوحظ عدم تاثير درجة الحرارة بشكل ملحوظ على النتائج, تم دراسة تاثير وزن القصب حيث وجد ان 0.4غم افضل وزن, كل هذه الظروف درست للقصب بحالته الطبيعية قبل المعاملة اما بعد المعاملة باليوريا والثايوريا اثبتت تحسن بالنتائج من 56% نسبة الازالة للقصب ثم 61% للمعامل باليوريا و68% للمعامل بالثايوريا. اما في حالة التجارب المستمرة فان النتائج بينت من خلال الرسومات ان نسبة الزيادة بالسرعة تؤدي الى انخفاض الكفاءة كذلك بالنسبة لزيادة التركيز بثبات وزن القصب يؤدي الى انخفاض الكفاءة. كذلك افضل منحنى تم الحصول عليه باستخدام قصب معامل بالثايوريا بوزن 2.5غم في معدل جريان مستمر حيث وجد ان منحنى الكفاءة ينحصر بوقت من 25دقيقة الى 175 دقيقة. تم تطبيق النتائج العملية على معادلات لانكماير وفرندليش واعطو تطابق للنتائج بمعدل تصحيح 0.971 للانكماير و0.9066 لفريندلش بالاضافة الى ان النتائج اظهرت تقاربا لمعادلة تفاعل من الدرجة الثانية بمعدل تصحيح 0.9941 بينما اعطت 0.136 لمعادلة من الدرجة الاولى.