DIVARATE NOVE COLUMN CONTRACT

Removal efficiency of copper (II) from aqueous solutions using Iraqi palm tree leaves

Salah A.Jassim

Rawnaq B.Gimaa

Nidhal M. Khames

Mohamed A. Farhan

Removal efficiency of copper (II) from aqueous solutions using Iraqi palm tree leaves

Salah A.JassimRawnaq B.GimaaNidhal M. KhamesMohamed A. FarhanDepartment of Chemistry- College of Science - University of Diyala

Received 19 June 2013; Accepted 2 February 2014.

<u>Abstract</u>

Iraqi palm tree leaves were used as biomass for removal of Cu^{+2} from aqueous solutions. Different parameters such as pH, biomass particle size, biomass weight and shaking time were studied in several batch wise experiments to obtain the optimal conditions for copper removal. Complete copper recovery (100%) was obtained and the maximum removal capacity of palm leaves ash (burned in 300 C°) was 25 mg/g. at pH=5. Comparisons of the results obtained by this method with comparable results in the literature were carried out proved the highly efficiency of this inexpensive biomass type in the decontamination of water contaminated with copper (which considered as toxic heavy metals) from industrial waste water before released to the river which represents the main source of drinking water.

Key word : Palm tree leaves, divalent copper, recovery, removal



Salah A.Jassim Rawnaq B.Gimaa Nidhal M. Khames Mohamed A. Farhan

كفاءة ازالة النحاس الثنائى من المحاليل المائية باستخدام سعف النخيل العراقي

صلاح الدين جاسم حمادي رونق بهمان جمعة نضال متعب خميس محمد علوان فرحان قسم الكيمياء – كلية العلوم -جامعة ديالي

الخلاصة

تم في هذا البحث استخدام سعف النخيل العراقي كمادة اولية في از الة النحاس الثنائي من محاليله المائية. تم در اسة مجموعة من المتغيرات في هذا البحث وتتضمن الدالة الحامضية pH، زمن المزج، حجم دقائق المادة الصلبة وتأثير اوز انها المختلفة على عملية الاز الة لتحديد الظروف المثلى للحصول على افضل از الة للنحاس بهذه المادة. بينت النتائج المستحصلة من هذا العمل على امكانية از الة النحاس بشكل تام وينسبة 100% وبسعة 25 ملغم من النحاس لكل غرام من مسحوق المعن والمحتوق المعن والمعنية المائي من محاليل والنها من المختلفة على عملية الاز الة لتحديد الظروف المثلى للحصول على افضل از الة للنحاس بهذه المادة . بينت النتائج المستحصلة من هذا العمل على امكانية از الة النحاس بقدة المادة . وينت النتائج مع من المحتول على المعن وتشعر المعن المادة . والمائل من المتحول على المحتول على المحتول المعل من المادة . والمائل المادة . والمائل المحتول على المحتول على المحتول المائل المادة . والمائل المحتول على المحتول المائل المائلة المائل المائل المحتول المائل المحتول على المحتول مائل المائل المائل المائل المائل المحتول المائل المحتول المائل المائل المائل المائل المائل المائل المائلة النحاس بهذه المادة . وينت النتائج المائل المحتول على المائل على المكانية از الة النحاس بشكل تام وينسبة 100% ويسعة 25 ملغم من النحاس لكل غرام من مائل والمحتوق المحتوق بدرجة 300 م⁰) في 5 pH - 3.

اجريت المقارنات بين نتائج البحث الحالي وبحوث عديدة اخرى والتي اثبتت الكفاءة العالية لهذا النوع الرخيص من المواد والمتاح بكثرة لغرض المعالجة المهمة لاز الة تلوث النحاس (كمعدن ثقيل سام) من المياه الصناعية قبل طرحها الى مياه الانهار التي تعتبر المصدر الرئيس لمياه الشرب.

الكلمات الدالة: سعف النخيل العراقى ، استرداد، از الة، النحاس الثنائي

Introduction

Heavy metals pollution is one of the most important environmental problems today. Huge amounts of heavy metals were released into the environment during industrial processing such as fertilizers and pesticides industry, energy and fuel production, surface finishing industry, electroplating, smelting and mining of metalliferous, leatherworking and other sources^{[1].}

Many agricultural wastes can be used as biomass for recovery of several heavy metals such as sawdust, rice husk pine bark, canola meal, sunflower stalks, date-palm leaf, tea waste, etc [2-4]



Salah A.Jassim Rawnaq B.Gimaa Nidhal M. Khames Mohamed A. Farhan

Date palm tree leaves are considered one of the most abundant in Iraqi country, they are available profusely over the course of the year, huge amounts of palm leaves are produced, that means these materials are very inexpensive, it is possible to take advantage of their chemical properties in metals recovery to be used for the removal of toxic heavy metals from drinking water and industrial waste water^[5]. Carbons are widely used to activate adsorption according to their ability to adsorb heavy metal ions. Carbonization is the term for the conversion of an organic substance into carbon, The adsorption capacities of carbonization products obtained at higher temperatures are higher than that of low temperature, they have a larger surface area and more suitable adsorption site^[6].

Large amounts of copper have been released to the environment during the operation of electrical and electroplating industries. In high level amounts, it is extremely toxic to living organism, Cu⁺² causes several toxicological effects to deposit in liver, brain, pancreas and myocardium^[7].

Using palm tree leaves as biomass for the treatment of metals contaminated wastewater to remove the toxicity of these materials from aqueous solution have been established by several researchers in this field ^[2,5,8,9]. Due to these references, metal removal percent and metal capacity has been calculated as following:

Removal (%) =
$$(C_o - C_e) / C_o * 100 \dots 1$$

q (mg/g) = $[(C_o - C_e) * V] / m \dots 2$

where q is the amount of copper ion recovery in (mg/g).

Ce the equilibrium concentration of ions after recovery in (mg/l).

- C_o initial concentration of ions in (mg/l).
- V is the initial volume of copper solution (L).
- m is the amount of dry added biomass in (g).





Removal efficiency of copper (II) from aqueous solutions using

Iraqi palm tree leaves

Salah A.Jassim

Rawnaq B.Gimaa

Nidhal M. Khames

Mohamed A. Farhan

Experimental

Reagents:

-Copper sulphate.5 hydrated, more than 99.8 purity, hemedia.

-Deionized Water

Equipment:

-Volumetric flasks (1000 and 25 ml).

-pH meter TWT 7110.

-Conical flasks (100ml).

-Eppendorf micropipette.

-Sensitive balance.

-Shaker Heidolph – unimax 2010.

-Atomic Absorption Spectrophotometer- Aurora –Canada.

- FTIR – perkin elmer.

Standard solutions:

Stock solution of divalent copper (1g/L) was prepared in deionized water. 100 mg/L standards solutions of Cu^{+2} were prepared daily by deionized Water dilution.

preparation of biomass:

Palm tree leaves were collected from diyala province in the middle of iraq, washed with distilled water and dried at $100C^{\circ}$. The leaves were powdered in a grinder and sieved to obtain the required particles size of 212 µm and 300µm both sizes were divided into two groups, the first group burned at 300 C°, then washed and filtered several times until the solution has been colorless followed by drying at 90C°, while the second group stay as it with out burning.

Batch experiments :

The experiments were established in rotary shaker at 300 rpm using conical flasks containing 25 m/L of 100 mg/L Cu^{+2} at room temp (all these parameters have been fixed in this study)



Salah A.Jassim Rawnaq B.Gimaa Nidhal M. Khames Mohamed A. Farhan

mixed with known amount of biomass. pH, biomass dosage, shaking time and particle size were variable parameters. After each run, the solutions were filtered and the filtrates were analyzed with atomic absorption to determine copper concentration. Removal % and removal capacity (q) were calculated using equation 1 and 2 respectively. FTIR also used to determine the active functional groups of the biomass.

Results and discussion

Effect of Dosage on removal of Cu⁺²

By agitating different amounts of palm leaves ash (0.02, 0.04, 0.06, 0.08, 0.1, 0.2, 0.3, 0.4 and 0.5 gm) with 25 m/L of 100 mg/L Cu⁺² at 3hr in 300 rpm with 300 μ m burned biomass. It can be seen from (fig-1) that the removal efficiency of Cu⁺² increases gradually until reaching the steady state at 0.1 gm, then completely removal has been achieved. According to eq.1, calculated removal capacity (q) was 25 mg Cu /g of leaves.

Effect of pH:

Agitation of various copper solutions over a pH range of 2 to 6 with 0.5 g of 212 μ m burnt and unburnt leaves were studied, fig 2 & 3 reflect significant improvements of copper removal efficiency between the two type of leaves which reaches about 99.1 % at pH \approx 6 for burnt leaves due to the high surface area produced by carbonization process, while the maximum removal value of unburned leaves was about 61% at the same pH. These results reflect highest activity of carbonized materials.

On the other hand, $300 \ \mu m$ of burned biomass was also used to evaluate its effects on copper removal efficiency, results shown in (fig-4) reflect highly efficient for copper adsorption (about 100%) was recorded.

Equilibrium Contact Time

For different period of contact time (5, 10, 20, 30, 60, 120, 180, 240 min), it can be concluded that after only 5 min, equilibrium would reach the steady-state. As shown in (fig-5) the trend of curve showed that removal percent attained the maximum after few min. and this result has been valuable compared with other studies on metals recovery field.



Salah A.Jassim

Rawnaq B.Gimaa

Nidhal M. Khames

Mohamed A. Farhan

Infrared analysis

To identify groups involved in the metal complexation and to provide acceptable explanation of recovery mechanism, Infrared analysis were carried out. FTIR spectra of palm leaves ash before and after copper binding are shown in fig (6). It is clear that primary amines are present due to the two N-H stretch absorptions at 3479 cm⁻¹ and 3416 cm⁻¹, in addition of N–H bend which appears at 1618 cm⁻¹. The band observed at 1221 cm⁻¹ could be assigned to the C–N stretch. Shifts in IR absorbance provide real evidence for specific interactions.

After binding with copper, significant shift at C-N stretching from 1221cm⁻¹ to 1147 cm⁻¹ confirms copper nitrogen binding in addition to N-H stretching band which shift from 3471 cm⁻¹ to 3479 cm⁻¹.

New absorbance band at 499 cm⁻¹ also appears which corresponded to M-N binding ^[19,20] and confirmed the suggested mechanism by finding the active site of biomass.

Comparison study:

According to obtained results from this work, comparison between copper removal percent of this study and by 11 references (included different biomass) were carried out.

As shown in table-1, the maximum removal efficiency of copper were obtained by reference ^[17] by using pretreated biomass of Fusarium Solana with aluminum hydroxide which reaches (96.53%) while completely copper recovery were established in this work compared with the all mentioned references.

On the other hand, recovery capacity (q) calculated in this work was 25 mg/g compared with ref^[8] which reaches 17.6 mg/g using the same material (palm leaves) but without carbonization process.



Salah A.Jassim

Rawnaq B.Gimaa N

Nidhal M. Khames

Mohamed A. Farhan

Conclusion

This study proved the practical and commercial feasibility of using palm leaves ash as inexpensive material for the treatment of copper contaminated wastewater.

The concluded optimum conditions from this study can be suggested as the following parameters:

Palm leaves ash burned at 300 C°.

Copper solution concentration = 100 mg/l.

pH =5.

mixing time = 1 hr.

shaking rate= 300 rpm.

particle size = $300 \mu m$.

According to these conditions, it is possible to treat 1000 L of copper waste solution by using only four kilogram as a palm powder on the ground that (q) calculated in this work equal 25 mg/g.

References

- 1. Kotrba, P., Mackova, M., Thomas Macek Microbial Biosorption of Metals, springer, 2011.
- 2. Ghorbania, F., Sanati, A. Younesi, M. H. and Ghoreyshi, A. A., *IJE. TRANS. B: App.*, 2012, 25(4) 296-278.
- **3.** Aikpokpodion, P. E., Ipinmoroti, R. R. and Omotoso, S. M., *Am. Eur. J. of Tox. Sci.* 2010, 2(2) 72-82.
- **4.** Lawrence, K., Ivanon, V., Hwa, J. and Tse, Y., Handbook of Environmental Engineering: Environmental biotechnology, 2010, Vol. 10, springer, London.
- 5. Kaakani, M. W., Heavy metal removal from waste water, A thesis in civil engineering, Sharjah, U.A.E, 2012.
- 6. Ozer, A. and Tumen, F., Europ. J. of Min. Process. and Env. Prot., 2005, 5(1), :.26-34.



Salah A.Jassim Rawnaq B.Gimaa Nidhal M. Khames Mohamed A. Farhan

- **7.** Lichtfouse, E., Schwarzbauer, J. and Robert, D., Environmental chemistry for a sustainable world, 2012, vol. 2: remediation of air and water, springer.
- 8. Hamdi, N., Abu Al-Rub, F., Kandah, M., Allaboun, H. and Hamdi, J., *Jord. J. of Civ. Eng.*, 2010, 4(3) :222-230.
- 9. Haleem, A. M. and Abdul gafoor, E. A., Al Kwar., *Eng. J.*, 2010, 6(4): 31 36.
- 10. Gopalakrishnan, K. and Jeyadoss, T., Ind. J. of Chem. Tech., 2011, 18(1): 61-66.
- 11. Al subu, M. M., Salam, R., Abu Shqair, I. and Swaileh, K. M., *Rev. Int. Contam. Ambient.*, 2001, 17(2): 91-96.
- **12.** Ganji, M. T., Khosravi, M. and Rakhshaee, R., *Int. J. of Env. Sci. & Tec.*, 2005, 1(4) :265-271.
- Popuri, S. R., Vijaya, Y., Boddu, V. M. and Krishnaiah A., *Bio. Tec.* 2009, 100(1) :194– 199.
- **14.** Karthika, T., Thirunavukkarasu, A. and Ramesh, S., *Res. in Sci. and Tech.*, 2010, 2(3) : 86–91.
- 15. Ilhan, S., Nourbakhsh, M. N., Kilicarslan S. and Ozdag, H., Turk. Elec. J. of Bioch., 2004, 2, : 50-57.
- 16. Wan Ngah, W. S. and Hanafiah, M. A., Biores. Techn., 2008, 99: 3935–3948.
- **17.** Bhatti, H. N., Samina, G. and Hanif, M. A., J. of the Chin. Chem. Soc., 2008, 55: 1235-1242.
- 18. Hossain, M. A., Ngo, H. H., Guo, W. S. and Nguyen, T. V., J. of Wat. Sust., 2012, 2(1): 87–104.
- 19. Onmmez, M. S., Turk. J. Chem., 2011, 25: 181 185.
- 20. Raj, G., advanced inorganic chemistry, 2010, vol.2, 12th ed., Mitra India.



Fig(2) Effect of pH on copper removal% using unburnt biomass (212 µm)





B- after binding with Cu(II)



Removal efficiency of copper (II) from aqueous solutions using

Iraqi palm tree leaves

Salah A.Jassim Rawnaq B.Gimaa	Nidhal M. Khames	Mohamed A. Farhan
-------------------------------	------------------	-------------------

biosorbent	Maximum Cu(II) Removal %	Biosorbent capacity mg/g	Reference
1 1 1	61		6
sugar beet pulp carbon	01		10
Activated rice husk	80%		10
Populus euphratica leaves	83%		11
treated Azolla filiculoides with 0.2 M. HCl	about 73%,		12
chitosan coated PVC beads	94%		13
Tridax procumbens	91%		14
Staphylococcus saprophyticus	14.5		15
Sulfuric acid poplar sawdust	92.4%		16
Pretreated Biomass of Fusarium solani by aluminium hydroxide	(96.53%)		17
Banana pell	96		18
Palm tree leaves (un burnt)		17.6	8
Palm tree leaves ash	100%	25	This study

