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Website: http://www.aun.edu.eg/faculty_agriculture *E-mail: ajas@aun.edu.eg*

Removal of Fe^{+3} and Cu^{+2} Ions from Aqueous Solutions by Adsorption Using Peanut Hulls

A.E. Awad

Agriculture Biochemistry Department, Faculty of Agriculture, Zagazig University, Zagazig 44511, Egypt

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Abstract

The present study was conducted to evaluate the possibility of using peanut hulls for the removal of $Fe^{+3}$and Cu^{+2} from aqueous solutions.This paper incorporates the effects of dose, concentration and pH.Adsorption of heavy metal on adsorbents was found to increase on decreasing initial concentration, the sorption capacity strongly increased with pH in the range 3-4. The results showed that the removal of heavy metals, such as $Fe^{+3}$and $Cu^{+2}$from aqueous solution was efficient using peanut hulls as bioadsorbent. The adsorption percentage of $Fe^{+3}$and Cu^{+2} ions by peanut hulls were very high. The Langmuir isotherm model was the best to describe the experimental data. The maximum sorption capacity was found to be 79.28 and 96.58 mg/g for Fe^{+3} and Cu^{+2}, respectively. Over all, the present findings suggest that peanut hulls are friendly environmental bioadsorbent, efficient and low cost biosorbent which represents an excellent potential for Fe^{+3} and Cu^{+2} removals from aqueous solutions.

Keywords: *Fe^{+3},Cu^{+2}, Peanut hulls, Scanning Electron Microscopy (SEM), Heavy metal removal, Biosorption, Langmuir isotherm model*

Introduction

Pollution from heavy metals has become a serious problem for human health and for environment. The heavy metals are not biodegradable and tend to accumulate in organisms causing various diseases (Inglezakis *et al.,* 2003). The existence of heavy metals, such as copper (Cu), ferric (Fe), nickel (Ni), zinc (Zn), lead (Pb), mercury (Hg), chromium (Cr) and cadmium (Cd) in wastewater, is the consequence of several activities like chemical manufacturing, paint pigments, plastics, metallurgy and nuclear industry (Quintelas *et al.,* 2009). Among various diseases associated to the presence of these toxic elements in the human body, there are neurotoxicity, severe gastro-intestinal irritation, and lung cancer (Jiang *et al.,* 2009 and Agouborde and Navia, 2009). The high heavy metals content in living organisms can cause serious health threats such as dullnedds, mental deficiency and irritability in humans (Naja and Volesky 2009).

Industrial and agricultural wastes pollute water with heavy metals, which reach tissues through the food chain (Florence, 1982 and Laxen, 1983). The toxicity of heavy metals to aquatic organisms has been a subject of interest to biologist for many years. Among different types of pollution the industrial wastes constitute the major sources of metal pollution. Toxic metals such as Cd, Zn, Cr, Pb, and Cu find their ways to the industries as metal plating industries, nickel batteries, pigments, and as stabilizers of alloys (Low and Lee, 1991).

For the removal of these metals from wastewater, there are a series of processes currently used for this object: chemical precipitation (Matlock *et al.,* 2001), hydroxide precipition (Huisman *et al.* ,2006) membrane filtration (Molinari *et al.,* 2004), sulfide precipition (Özverdi and Erdem, 2006 and Kousi *et al.,* 2007) electrolytic reduction (Beauchesne *et al.,* 2005), solvent extraction (Silva *et al.,* 2005), ionic exchange (Pehlivan and Altun, 2007 and Motsi *et al.*,2009) chelating precipition , (Fu *et al.*, 2007) and adsorption (Ajmal *et al.,* 1998 and Ronda *et al.,* 2013), reverse osmosis (Dialynas and Diamaolopoulos, 2009) and nanofiltration (Figoli *et al.*, 2010), electrodialysis, (Cifuentes *et al.,* 2009), coagulation and flocculation (Duan *et al.*, 2010).

Agricultural waste is one of the rich sources of low cost adsorbents apart from industrial by-products and natural materials. Due to its abundant availability agricultural waste such as peanut husk, rice husk, wheat bran and sawdust offer very little economic value and, moreover, create serious disposal problems (Li *et al.,* 2013 and Zafar *et al.,* 2015). Activated carbons derived from peanut husk and rice husk have been successfully employed for the removal of heavy metals from aqueous solutions (Liao *et al.,* 2011). The use of peanut hulls carbon (PHC) for the adsorption of Cu^{+2} from wastewater was studied by Periyasamy and Namasivayam, (1996); their comparative study of commercial granular activated carbon (GAC) showed that the adsorption capacity of PHC was 18 times larger than that of GAC**.**

Adsorption is now recognized as an effective and low cost method for heavy metal wastewater removal (Fenglian and Wang, 2011). They reviewed several processes of adsorption, i.e. active carbon adsorbents (Kang *et al.,* 2008), carbon nanotubes (Li *et al.*, 2010), low cost adsorbents (Jiang *et al.*, 2010 and Krika *et al.,* 2016).

Peanut (*Arachis hypogea* L.) is an important oilseed crop. It is not only important for the production of oil, but also for direct consumption. They are consumed raw, roasted, pureed, or mixed with other foods or in different processed forms of which peanut butter is the most important. Recently, peanuts have gained much attention as functional food (Fransisco and Resurrection, 2008). Peanut shells and skins are usually removed before processing or even when eaten as condiment.Shells and skins are sometimes burned or used in animal feed or as organic fertilizers. Peanut skin, shell, and kernel extracts were reported to exhibit different levels of antioxidant activity (Duh and Yen, 1997 and Talcott *et al.,* 2005).

Copper is a common pollutant among these toxic metals that is widely used in many industries, having numerous opportunities to make its way into wastewater and natural waters (Ronda *et al.*, 2013).

The aim of the present study is to evaluate peanut hulls as a potential adsorbent for Fe^{+3} and Cu^{+2} removals from aqueous solution. The adsorbent-adsorbate equilibrium behavior has been investigated using Langmuir isotherms.

Materials and Methods

Adsorbents

Peanut (*Arachis hypogea* L.) collected from the local market of Zagazig, Egypt. Peanuts were washed several times with distilled water to remove dirt particles. The wetted peanut hulls were air dried at room temperature and then oven dried at 105°C for 24 hours. The dried peanut hulls were ground into a powder and sieved to pass through 60 mesh screen, kept in an air tight bottle for experimental use.

Absorbate

A standerd stock solutions of ($FeCl_3.6H_2O$) and Copper sulphate ($CuSO_4.5H_2O$) were prepared (1000 mg/l) and used for all experiments with required dilution with distilled water.

Methods

Chemical composition of peanut hulls

Moisture, crude fat, crude protein, ash, crude fibre, cellulose and hemicellulose contents were determined in peanut hulls, according to A.O.A.C. (2005).

Adsorbent dosag

The effect of adsorbent dosage on the equilibrium adsorption of heavy metal ions were investigated with peanut hulls of 0.1, 0.25, 0.5and 1g in five sets of 100 ml water which contained 50,100,500,1000 mg/l of heavy metal concentration each. The Erlenmeyers were shaken for 24 hours with 150 rpm at room temperature. Then, the samples were filtered. Fe^{+3} and Cu^{+2} concentrations in filterate were determined by Atomic Absorption Spectrometer (AAS).

Study the effect of pH

The effect of pH for tested heavy metals adsorption onto peanut hulls was investigated with 0.5g of peanut hulls in 100 ml water containing 100mg/l of heavy metal ions and each sample were adjusted to pH between 2.0 to 8 using either 1N HCl or NaOH solution. The biomass was separated from the solution by filteration and the resulting solutions were analyzed for Fe^{+3} and Cu^{+2} by Atomic Absorption Spectrometer.

Equilibrium study

Equilibrium adsorption experiments (triplicates) were conducted with 16 Erlenmeyer of 100 ml water containing 1 to 1000 mg/l of Fe^{+3} and Cu^{+2} concentrations. Ground peanut hulls of 0.1, 0.25 and 0.5 g were added in each sets of experiments and shaken for 24 hours with 150 rpm at room temperature without pH adjustment.The equilibrium data were fitted with Langmuir isotherm models.

Analysis

The collected water samples from different experiments were filtered with filter paper (Whatmann 1) and prepared for AAS analysis. The samples were analyzed in term of heavy metal ions by Atomic Absorption Spectrometer (Thermo scientific Ice 3000). The pH was measured by pH meter.The amount of metal ions adsorbed was determined by difference between the initial and final concentrations. The sorption efficiency (%) and amounts of adsorbed metal (qe) by hulls were calculated using the following equations:

$$(1)\ \text{Removal efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100$$

$$(2)\ q_e = \frac{(C_0 - C_e)\,V}{m}$$

Where: C_0 and C_e (mg/l) are the liquid-phase concentrations of metal initially and at equilibrium, respectively. V is the volume of the solution (l), m is the mass of adsorbent (g) and q_e (mg/g) is the amount of adsorbed metal at equilibrium (Ossman *et al.,* 2014).

Langmuir isotherm

The Langmuir isotherm applies to adsorption on completely homogenous surfaces with negligible interaction between adsorbed molecules. The form of Langmuir (Duddridge and Wainwright, 1981) was used to describe adsorption isotherms.

The Langmuir isotherm equation is:

$$q = q_{max} \cdot \frac{b\ Cf}{1 + b\ Cf}$$

Where q is the metal uptake by peanut hulls (mg/g), q_{max} is the maximum amount of heavy metal adsorbed on the adsorbent (mg/g^{-1}), Cf is the equilibrium concentration of metal in solution (mg/l), (b, q_{max}) is empirical constant of Langmuir isotherms.

Scanning Electron Microscopy (SEM)

The Scanning Electron Microscopy (SEM), Model: Hitachi SU-1500 was used for the study of peanut hulls structure. The micrographs obtained before and after the adsorption of metal ions were compared to study the adsorption efficiency. Data size was 1280 x 960, accelerating voltage 15000 V, deceleration voltage was 0V and emission current was 86000 nA. SEM analysis was used for the study of peanut hulls structures using high magnification, (Zhu *et al.,* 2013).

Results and Discussion

Chemical composition of peanut hulls

The chemical composition of peanut hulls is summarized in (Table 1). Data showed that peanut hulls composition was, organic matter 92%, ash content 3.8%; crude protein 5.4%; crude fat 0.1%; lignin 36.1%; hemicellulose 5.6% and cellulose 44.8%. The obtained results are in accordance with those of (Brown *et al.,* 2000 and Yang *et al.,* 2005). Basso *et al.,* (2002) who reported that there was a correlation between lignin content of several lignocelluloses and their ability to remove heavy metals from aqueous solutions, therefore the high content of cellulose and lignin observed in the tested peanut hulls favour biosorption of metal ions. Moreover, lignocellulosic materials are very porous, have a very high specific surface area and affinity for water (Pehlivan *et al.,* 2008), which improve the performance of these materials as sorbents. Cellulosic surface becomes partially negatively charged when immersed in water so that possesses columbic interaction with cationic species, which contributes to the high binding abilities of these materials, especially divalent metal cations (Laszlo and Dintzis, 1994). The oxygen of each carbonyl (present in fats, lignin, protein and pectin) and hydroxyl group (present in cellulose and lignin) are considered a strong Lewis base because of the presence of its vacant double electrons, which could bind to a metal cation forming a complex of coordination.

Table 1. Chemical composition of peanut hulls

Componentes	Organic Matter	Ash Content	Crude Protein	Crude Fat	Lignin	Hemicellulose	Cellulose
Concentration %	92	3.8	5.4	0.1	36.1	5.6	44.8

Effect of pH

The adsorption of Fe^{+3} and Cu^{+2} ions is strictly pH dependent. Results of the experiments using 100 mg/l heavy metal ions solutions and 10 g/l adsorbent showed that efficiencies of adsorption were increased for both adsorbents with increasing pH from 2.0 to 8.0. The results presented in Figure (1) show the effect of pH on Fe^{+3} and Cu^{+2} removals. The sorption capacity strongly increased with pH in the range 3-4. The same effect was observed by Zhu *et al.,* (2008) who explained that it is because the point of zero charge for peanut hulls is about 3.5. At pH values higher than 4, the change in capacity values was not significant for copper and iron. The pH value between 5 and 6 was considered the most favorable for all systems according to the results presented in Figure 1. These findings were also reported in the cited studies for metal divalent ions removal using agricultural wastes. At pH values above 6.0, heavy metal ions adsorption was increased. This can be explained by the precipitation of Fe^{+3} and Cu^{+2} ions in the solution. At the optimal pH of 6.0, 74% and 62% of Fe^{+3} and Cu^{+2} ions were removed by peanut hulls,respectively Similarly, Basci *et al.,* (2004) and Waseem *et al.*, (2014) reported that pH has a significant role on heavy metal ions removal.

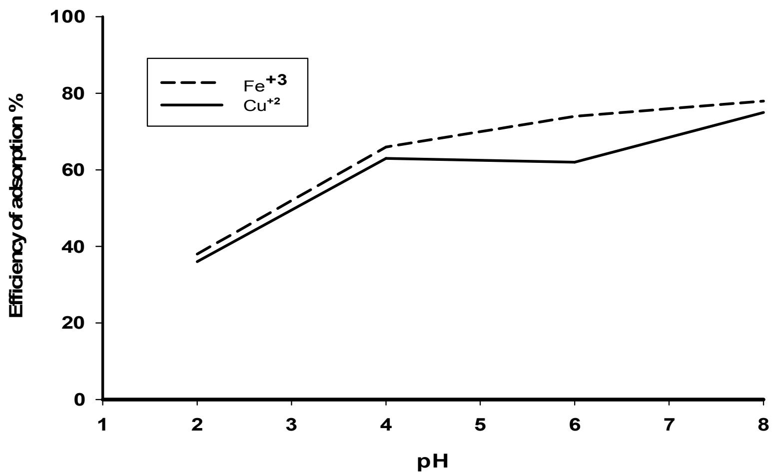


Fig. 1. Effects of pH on adsorption of Fe^{+3} and Cu^{+2} on peanut hulls at 30°C, 150 rpm shaking, amount of adsorbent 0.5g/l00ml and the contact time 1h.

Effect of adsorbent dosage

Dose dependent experiments show that copper removal was low at lower doses and gradually increased with increasing in doses (Figure 2). The highest heavy metal ions removal (79%) for iron and (73%) for copper was obtained by the initial heavy metal ions concentration of 100 mg/l and adsorbent dose of 10g/l. The partial aggregation among the available active binding sites at higher doses and lack of active binding site at lower doses retards the copper adsorption onto peanut hulls (Karthikeyan *et al.,* 2007 and Anwar *et al.,* 2010).

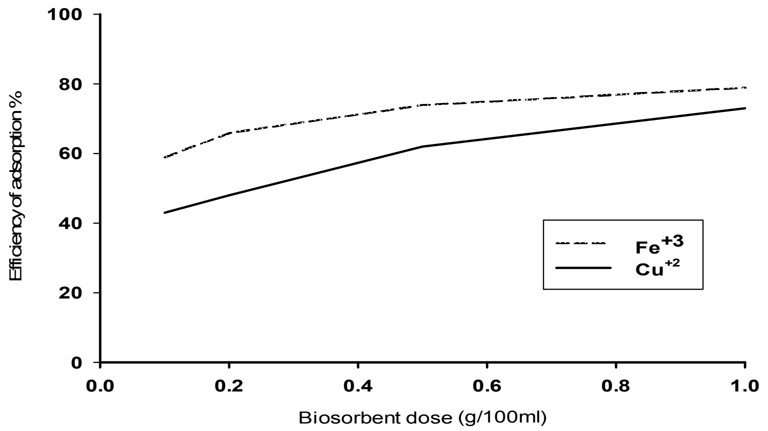


Fig. 2. Effects of adsorbent dosage on adsorption of Fe^{+3} and Cu^{+2} (100 mg/l) on peanut hulls at 30°C, 150 rpm shaking, pH 5.0 and the contact time 1h.

Effects of initial heavy metal ions concentration

The effect of various initial concentrations of Fe^{+3} and Cu^{+2} on the removal efficiency of Fe^{+3} and Cu^{+2} is shown in Fig. 3. Results indicate that the adsorption of Fe^{+3} and Cu^{+2} by peanut hulls was studied at different copper and iron concentrations in the range from 50 mg/l to 1000 mg/l. Adsorption efficiencies decreased with the increasing of the copper and iron concentration at constant adsorbent amount 10g/l. (Ma and Tobin 2004) reported that sorption of Cu^{+2} from aqueous solutions was increased with increasing solution concentration (5-200 mg/l) at amount of adsorbent 1g/l.This demonstrate that the adsorbed amount of both heavy metals by the peanut hulls dependent upon availability of binding sites for Fe^{+3} and Cu^{+2}.

The removal efficiency of heavy metals was the highest at 50 mg/l for Fe^{+3} and Cu^{+2}.

Similar trend was reported by (Javadian *et al.,* 2015) and Ali *et al.,* (2014). The later reported that increasing the initial Cu^{+2} concentration above 250 mg/l led to decline the percent adsorption of Cu^{+2} indicating saturation of all the binding sites on peanut hulls, surface beyond a particular concentration and establishment of equilibrium between adsorbate and adsorbent (Malkoc 2006 and Ozturk *et al.,* 2004).

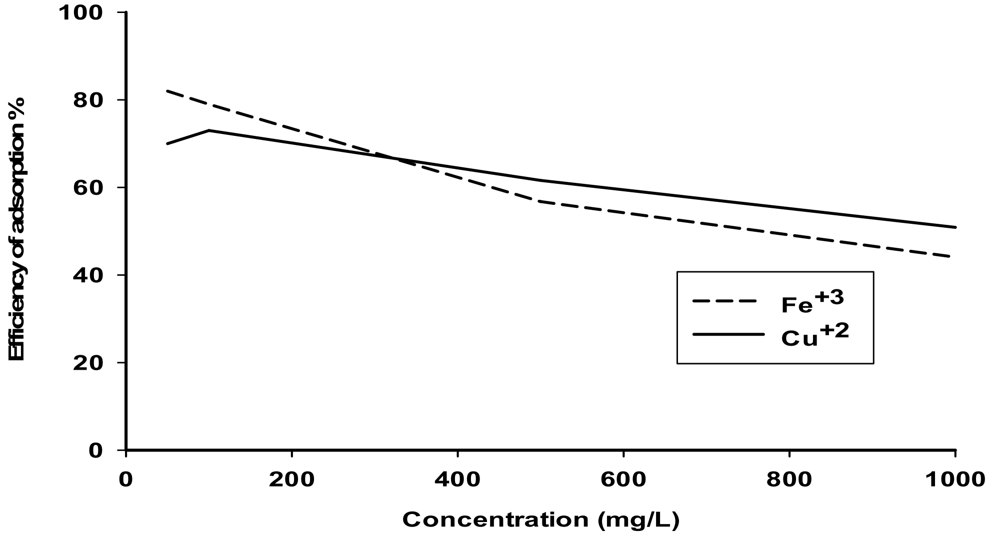


Fig. 3. Effects of initial metal concentration on adsorption of Fe^{+3} and Cu^{+2} on peanut hulls, (Peanut hulls concentration was 1g/l, pH =5.0 Contact time was 1h.)

Langmuir adsorption isotherm model

The Langmuir adsorption isotherm model has been usually selected to study the adsorption principle and capacity. Constant values in model can express the surface properties and affinity of peanut hulls and also be used to compare the biosorptive capacities of peanut hulls for Fe^{+3} and Cu^{+2}. In this study, Langmuir adsorption isotherm model was used to fit experimental data. Constant values in models were listed in Table (2).

Generally, when correlation coefficients (R^2) is greater than 0.95, the biosorption isotherm model is thouught to be established. According to Table (2), obviously, Langmuir isotherm model described a better adsorption process. In the Langmuir isotherm model, b and q_{max} are Langmuir constants, related to the binding constant and the maximum adsorption capacity, respectively. The higher q_{max} value means stronger adsorption capability of biosorbent. In this study, the q_{max} value, the maximal metal uptakes (q_{max}) of peanut hulls were 79.28 and 96.58 mg/g for Fe^{+3} and Cu^{+2}, respectively. This ruselt is in the same line with (Ossman 2014) who stated that Langmuir adsorption isotherm describes the case of adsorption on peanut shell very well.

Table 2. Langmuir isotherm constants for the biosorption of Fe^{+3} and Cu^{+2} on peanut hulls

Heavy metal ions	Langmuir		
	b	q_{max}	R^2
Fe^{+3}	0.036	79.28	0.9801
Cu^{+2}	0.028	96.58	0.9763

Table 3. The adsorption capacity of Fe^{+3} on different adsorbents

Types of adsorbent	q_{max} (mg g -1)	References
Hazelnut hulls	13.59	Sheibani *et al*., 2012
Cow bone charcoal	32.54	Moreno, *et al*., 2010
Green micro	63.09	Kondo, *et al*., 2012
Wood sawdust	32.76	Ahmed,2011
Polisher resin	36.50	Aboul.Magd *et al*., 2016
Modified chitosan heads	4.88	Gandhi *et al*., 2012
Natural zeolite	1.11	Shavandi *et al*., 2012
Nano hydroxyapatite	12.11	Kousalya *et al*., 2010
Chitosan(ECH)	72.46	Nagah *et al*., 2005
Chitosan(GLA)	51.55	Nagah *et al*., 2005
Chitosan(EGDE)	46.30	Nagah *et al*., 2005
Chitosan(CTS)	0.97	Zou *et al*., 2011
Attapulgite (Atp)	9.2	Zou *et al*., 2011
Chitosan/ Attapulgite	36.76	Zou *et al*., 2011
Peanut hulls	79.28	Present work
Rice husk	68.59	Hala Hegazi, 2013
Fly ash	46.18	Hala Hegazi, 2013

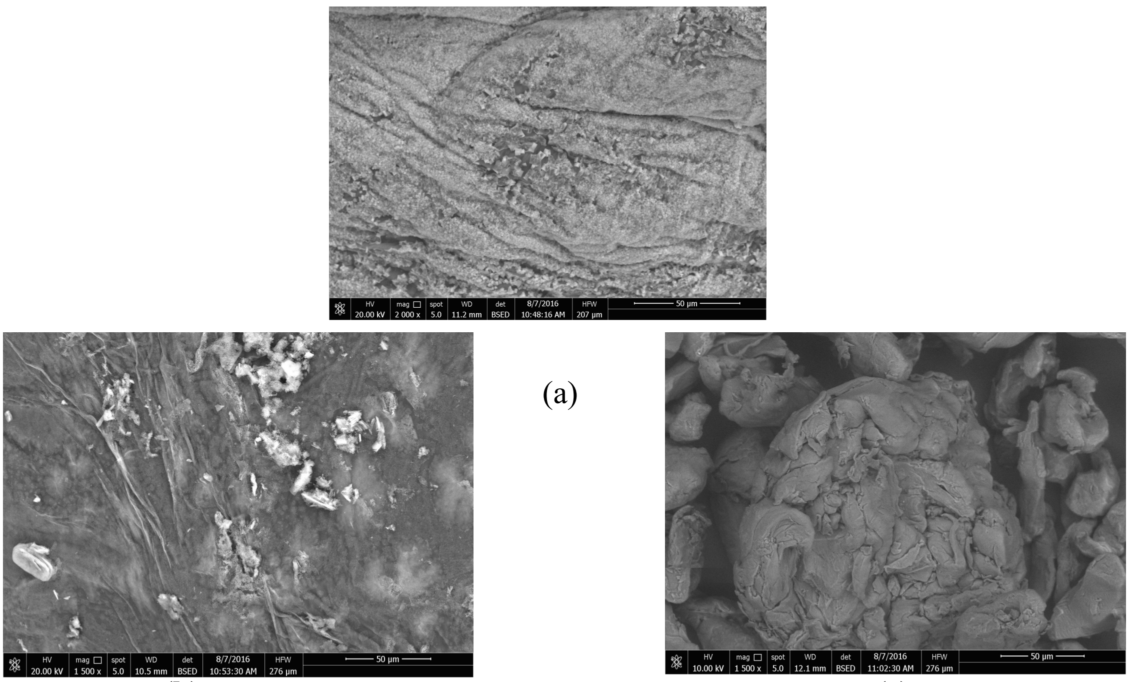
Table 4. The adsorption capacity of Cu^{+2} on different adsorbents

Types of adsorbent	q_{max} (mg g^{-1})	References
Cotton boll	11.4	Ozsoy and kumbur 2006
Papaya wood	19.8	Saeed *et al*., 2005
Chitosan alumina	86.2	Boddu *et al*., 2008
Chitosan PVC	87.9	Popuri *et al*., 2009
PET-AA-CS	68.9	Niu *et al*., 2016
Pecan shells activated carbon	31.7	Bansode *et al*., 2003
Ecklonia maxima	90	Fenga and Aldrich , 2004
Rice husk	24.49	Hala Hegazi, 2013
Fly ash	37.38	Hala Hegazi, 2013
Zeolite	1.64	Babel and kurniwan, 2003
PET fiber	1.92	Yigitoglu *et al*., 1998
PET	7.7	Coskun *et al*., 2006
Hcl – treated clay	83.3	Vengris *et al.,* 2001
CNTS immobilized by calcium alginate	79.9	Li *et al* .,2010
PEUF	94	Molinari *et al*., 2008
Nf	47	Chaaban *et al*., 2006
Peanut hulls	96.58	Present work

The maximum adsorpation capacity is compared in Table (3) and Table (4) with the data reported by other researchers for Fe^{+3} and Cu^{+2} biosorption. It can be seen that the maximum Fe sorption value by peanut hulls is higher than those reported in the literature where the value of q_{max} for Fe by peanut in this work represents 79.28% and that indicates the great potential of peanut hulls as low cost adsorbent material for the removal of Fe ions from waste water. In addition, comparing the values of adsorption capacity of Cu ions with data reported by other authors as can be seen, the maximum Cu^{+2} sorption value (96.58) of peanut is higher than those obtained in the literature. The comparison shows the great potential of peanut hulls for removal of copper ion from waste water, taking the same trend of Fe^{+3}. HalaHegazi, 2013 investigated rice husk and fly ash as adsorbent for Fe^{+3} and Cu^{+2} from aqueous solution and other researchers investigated modified agro waste materials as adsorbent for Fe^{+3} and Cu^{+2} removal from aqueous solutions (Bansode *et al.,* 2003, Saeed *et al.*, 2005, Ozsoy and kumbur 2006, Ahmed, 2011 Kondo *et al.,* 2012). Results of these studies indicate that adsorption efficiency for peanut hulls is higher in comparison with treated agro waste materials (Tables 3 and 4). Accorbingly, It could be concluded that peanut hulls according to these data represents an excellent potential adsorbent for removal of Fe^{+3} and Cu^{+2} from waste water.

Scanning Electronic Microscopy (SEM)

The microporous structure of peanut hulls with particle sizes of 150-212 µm was observed at a resolution of 500x (Figure 4). The micrograph of biosorbent shows some cavities in the surfaceûs structure capable of uptaking heavy metal ions as well as an irregular and porous microstructure of the biosorbent. It is clearly seen that there is a considerable modification on morphology of biosorbent before and after heavy metal ions binding. Satish (2015) also explianed the surface morphology of peanut hulls (*Arachis hypogaea* L.) using Scanning Electron Microscope (SEM), before and after adsorption and the corresponding SEM micro graphs were obtained accelerating voltage of 10.0 kv at 15000x for before and 1500x for after adsorption magnification. At such magnification, the peanut hulls (*Arachis hypogaea* L.) particles showed rough areas of within which micro pores were clearly identified.



(a)

(b) **(c)**

Fig.4. SEM micrograph of (a), peanut hulls befor biosorption of heavy metal ions. (b), after biosorption of ferric ions. (c), after biosorption of copper ions

Conclusion

Peanut hulls are a high capacitate, economically viable and low cost adsorbent for heavy metal ions removal from waste water. The adsorption capability of peanut hulls for Fe^{3+} and Cu^{2+} was affected by pH and initial peanut hulls concentrations and metal concentrations. Adsorption of ferric and copper on peanut hulls shows high association with Langmuir isotherm model. This result indicated that the metals adsorption capacity was in the sequence: Cu^{+2}> Fe^{+3}.

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Website: http://www.aun.edu.eg/faculty_agriculture *E-mail: ajas@aun.edu.eg*

ازالة كلا من ايونات الحديد والنحاس من المحلول المائي بالادمصاص باستخدام اغلفة الفول السوداني

أحمد السيد عوض محمد

قسم الكيمياء الحيوية الزراعية – كلية الزراعة – جامعة الزقازيق – مصر

الملخص

يهدف البحث الي امكانية استخدام اغلفة الفول السوداني لازالة كلا من ايونات الحديد والنحاس من المحاليل المائية وذلك بدراسة تاثير كلا من كمية المادة وتركيز العنصر ودرجة الحموضة. ادمصاص العناصر الثقيلة علي المادة المستخدمة زاد زيادة واضحة في مدي درجة حموضة ٣ الي ٤ واظهرت النتائج ان ازالة العناصر الثقيلة المتمثلة في الحديد والنحاس كانت بكفاءة عالية باستخدام اغلفة الفول السوداني كمادة بيولوجية لها القدرة علي الادمصاص ولذا اظهرت النتائج ادمصاصا كبيرا لكلا من الحديد والنحاس وقد استخدم نموذج لانجمير للادمصاص لتاكيد وتفسير القدرة علي الادمصاص وهذا وقد كان اقصي معدل ادمصاص هو ٧٩,٢٨ و٩٦,٥٨ ملليجرام/ جرام لكلا من الحديد والنحاس علي التوالي. هذا ويوصي هذا البحث ان اغلفة الفول السوداني تعتبر مادة صديقة للبيئة وذات كفاءة عالية لادمصاص العناصر الثقيلة علاوة علي ذلك فهي رخيصة الثمن.