

Removal of Copper (II) and Ferric (III) Ions from Aqueous Solutions by Adsorption Using Potato Peel



El-Maghraby, Lamiaa M.M.

Agric. Biochemistry Dept., Fac. of Agriculture, Zagazig University, Zagazig, Egypt
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Abstract

In this work, potato peel wastes were used as absorbents to remove heavy metals (Cu^{+2} and Fe^{+3}) from aqueous solutions using adsorption method. Effect of pH, contact time, adsorbent dosage and initial metal pollutants concentration was investigated. Results showed that the adsorption of Cu and Fe ions increased with increasing pH of media and maximum adsorption of both Cu and Fe was obtained around pH 5 - 6. The maximum sorption capacity was found to be 39 and 28 mg/g for Cu^{+2} and Fe^{+3} , respectively. Over all, the present findings suggest that potato peels are friendly environmental, efficient and low cost biosorbent which represents an excellent potential for Cu^{+2} and Fe^{+3} removals from aqueous solutions.

Keywords: Adsorption, Heavy meta, Potato peel, Copper, Ferric.

1. Introduction

Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 (Srivastava *et al.*, 2008). With the rapid development of industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides, etc., heavy metals wastewaters are directly or indirectly discharged into the environment increasingly, especially in developing countries.

Heavy metals in the aquatic medium may originate from wastewater of many industries, such as batteries, tanneries, electrical, electroplating, fertilizers, pesticides, mining, refining ores, etc. (Banerjee *et al.*, 2012; Manzoor *et al.*,

2013). Due to their hazardous effects, persistency and accumulation tendency, heavy metals can pose a risk to the human and environmental health (Kumar *et al.*, 2012; Marin *et al.*, 2010). The exposure to heavy metals can cause damage to many parts of human bodies, even at very low concentrations. Therefore, the removal of heavy metals from aqueous solutions is of extreme importance. The United States Environmental Protection Agency (USEPA) has set up the maximum contamination levels (MCLs) of heavy metals for surface or groundwater to be used in the drinking supply. Table 1 describes the typical poisoning symptoms and MCLs of the most common heavy metals (Barakat, 2011).

Table 1. The maximum contaminant levels (MCL) for the most common heavy metals.

| Heavy metal | Toxicities | MCL (mg/L) |
|----------------------|---|------------|
| Arsenic (As) | Skin manifestations, visceral cancers, vascular disease | 0.05 |
| Cadmium (Cd) | Kidney damage, renal disorder, human carcinogen | 0.01 |
| Chromium (Cr) | Headache, diarrhea, nausea, vomiting, carcinogenic | 0.05 |
| Copper (Cu) | Liver damage, Wilson disease, insomnia | 0.25 |
| Nickel (Ni) | Dermatitis, nausea, chronic asthma, coughing, human carcinogen | 0.20 |
| Zinc (Zn) | Depression, lethargy, neurological signs and increased thirst | 0.80 |
| Lead (Pb) | Damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system | 0.006 |
| Mercury (Hg) | Rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system | 0.00003 |

Copper is generally considered highly harmful metal at high concentration. It's an essential element needed by humans and plays a vital role in enzyme synthesis, bone development. The different copper forms in the environments are Cu (metal), Cu⁺ (cuprous ion), Cu²⁺ (cupric ion). The Cu²⁺ is found to be more toxic in the environment. The effect of copper takes place in liver, brain, pancreas and leads to death (Carolin *et al.*, 2017).

Feizi and Jalali (2015) indicated that the plant residues showed considerable capacity for removal of heavy metals (Fe, Mn, Zn, Cu and Cd) from aqueous solution but Ni sorption by residues was negligible.

Potato is a crop that is native to tropical America and its one of the major root and tuber crops in the tropical regions of the world. It is widely grown and consumed as a staple food in many parts of Africa, Latin America, Asia and the Pacific Islands (FAO, 1998). It is the tenth major crop in world with a global output of about 100 million tonnes per year, Nigeria is second largest producer after China with a reported annual output of 2.83 million tonnes in 2010 (Unctad, 2012)

and 3.45 million tonnes in 2013 (Faostat, 2015). In Nigeria, sweet potato is grown for both human and animal consumption and it is consumed in the boiled form after it has been peeled (Egbe *et al.*, 2012 and Olagunju *et al.*, 2013). The peel has no significant application and is mainly used as animal feed though the generation capacity outstrips animal consumption in many areas of the country thereby leading to a waste management problem.

Potato peel waste is a non-edible residue generated considerable amounts by food processing plants. Depending on the peeling process, i.e. abrasion, steam or lye peeling, the amount of waste can range between 15 and 40% of the amount of processed potatoes (Arapoglou *et al.*, 2010). Most of the potato peel is discarded (Chen *et al.*, 2012) and only a low amount of it is used as a supplementary animal feed, fertilizer or is composted (Israilides *et al.*, 2008). Potato peel from the abrasion peeling process contains a large quantity of starch, e.g. 52% (dry basis) (Camire *et al.*, 1997). Starch is globally the second most abundant carbohydrate. After various modifications, it is largely used in industrial applications

and is a potential resource for bio-energy production. The use of PW for chemical modifications of starch would promote the material efficiency and the sustainable use of natural resources.

The process of adsorption on natural adsorbents (bio sorption) is relatively recent process is a great application in the removal of inorganic and organic pollutants from waste water. Adsorption on bio sorption has become a potential alternative to existing technologies for the effective removal of low concentration of Cu^{+2} and other metals from aqueous solution and waste waters because of the simplicity, cost-effectiveness and high capacity of removing pollutants (Krstic *et al.*, 2018).

Burakova *et al.* (2018) reported that adsorption method is one of the most efficient techniques for removing noxious heavy metals from the solvent phase using various adsorbents conventional (activated carbons, zeolite, clays, bio sorbents and industrial byproducts) and nanostructured (carbon nanotubes and graphenes).

In this study, potato peel was used for removal of copper and ferric ions from aqueous solutions by the batch method. Effective parameters such as initial pH of the metal solutions, initial metal concentrations and potato peel dosage were investigated.

Materials and Methods

Adsorbents

Potato peels (*Solanum tuberosum* L.) were collected from chips manufacturing industry from the Chips Factory of City 10th of Ramadan; Sharkia Governorate. Potato peels were washed several times with

distilled water to remove external dirt particles. The wetted potato peels were air dried at room temperature and then oven dried at 105°C for 24 hours. Samples of potato peels were ground into a powder and sieved to pass through 60 mesh screen, kept in an air tight bottle until use.

Absorbate

Standard stock solutions of copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were prepared (1000 mg/l) and used for all experiments with required dilution with distilled water.

Methods

Chemical composition of potato peels

Moisture, crude fat, crude protein, ash, crude fiber, cellulose and hemicellulose contents were determined in potato peels, according to A.O.A.C. (2005).

Adsorbent dosage

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

Effect of pH

Effect of pH for tested heavy metals adsorption onto potato peels was investigated with 1g of potato peels in 100 ml water containing 100mg/l of heavy metal ions and each sample was adjusted to pH between 2.0 to 8 using either 1N HCl or

NaOH solution. The biomass was separated from the solution by filtration and the resulting solutions were analyzed for Fe^{+3} and Cu^{+2} by Atomic Absorption Spectrometer.

Effect of initial ion concentration

Equilibrium adsorption experiments (triplicates) were conducted with 100 ml water containing 1 to 1000 mg/l of Fe^{+3} and Cu^{+2} concentrations. Ground potato peels of 1 g were added in each sets of experiments and shaken for 24 hours with 150 rpm at room temperature with pH 5.

Analysis

The collected water samples from different experiments were filtered with filter paper (Whatmann 1) and prepared for AAS analysis. 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 (q_e) 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).

Results and Discussion

Chemical composition of potato peel

The chemical composition of potato peel allowed the determination of the following parameters (Table 2): potato peel contained 7.89% moisture, 9.32% ash, 12.45% crud protein, 1.4 % crud fat, 33.4 % lignin, 5.3% hemicellulose and 4.2% of cellulose. The result is in close agreement with María *et al.*, (2018) who stated that dry potato peel contained 5.26% moisture, 7.45% ash, 2.45 % crud fat, 32.88% lignin, 7.41% hemicellulose and 8.3% cellulose. Basso *et al.* (2002) suggested that there was a correlation between lignin content of several lignocelluloses and their ability to remove heavy metals from aqueous solutions. Therefore the high cellulose and lignin content observed favor biosorption of metal ions. 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).

Table 2. Chemical composition of dry potato peel

| Componentes | Moisture | Ash | Crude Protein | Crude Fat | Lignin | Hemicellulose | Cellulose |
|-----------------|----------|------|---------------|-----------|--------|---------------|-----------|
| Concentration % | 7.89 | 9.32 | 12.45 | 1.4 | 33.4 | 5.3 | 4.2 |

Effect of adsorbent dosage

The detailed results of the kinetic experiments with varying adsorbent concentration were presented in Fig. 1. It is clearly show that the amount of metal ions adsorbed varied with the potato peel concentration. The degree of adsorption increased with an increase in the amount of adsorbent in solution and equilibrium. The higher degree of adsorption can be related to the increase in adsorption sites with the increase in the adsorbent masses (Benguella and Benaisa, 2002). Fig. 1 shows the percentage removal of copper (II) and ferric (III) at a concentration of 100 mg /l. It is evident that the percentage removal of copper (II) increases from 45% to 85% with the increasing adsorbent concentration. The best economical adsorbent concentration was

chosen to be 1% (w/v). The observed trend can be attributed to the fact that, initially with an increase in adsorbent dosage, more number of active sites are available which coupled with higher surface area of the adsorbent facilitates the increase in the extent of adsorption. This means that almost all ions are bound to the adsorbent and equilibrium is reached between the ions bound to the adsorbent and those remaining unadsorbed in the solution in a faster time interval (Gutha *et al.*, 2011 and Dubey and Shiwan, 2012). Another reason to reduced removal efficiency at the higher loading of the adsorbents is the overlapping of adsorption sites due to the possible aggregation of the adsorbent particles leading to a decrease in the total surface area. Similar trend was observed by Boota *et al.* (2009).

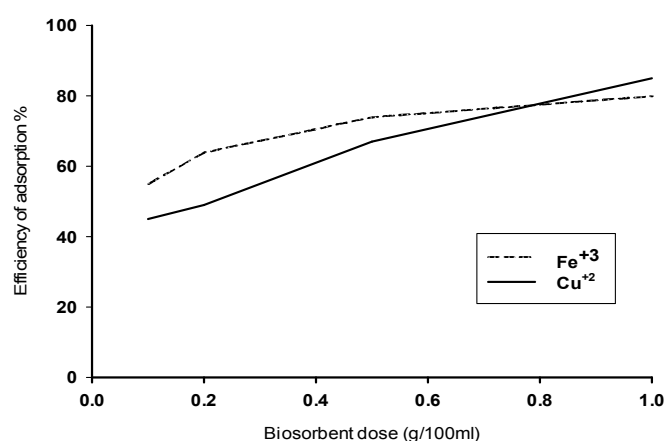


Fig. 1. Effects of adsorbent dosage on Fe⁺³ and Cu⁺² (100 mg/l) adsorption on potato peel at 30°C, 150 rpm shaking, pH 5.0 and the contact time 1h.

Effect of pH

The pH of the solution is an important factor in the adsorption process, which affects surface charge of the adsorbent, the degree of ionization and speciation of adsorbate. The pH dependency of adsorption could be explained based on the involvement of functional groups in metal uptake and metal chemistry (Kumar *et al.*, 2011). In this experiments 100 mg/l heavy metal ions solutions used and 10g/l adsorbent showed that efficiencies of adsorption were increased for both adsorbents with increasing pH from 2.0 to 8.0. The effect of initial pH on the adsorption process is presented in Fig. 2. As seen in Fig. 2, the adsorption percent of Cu (II) and Fe (III) increased with increasing pH and maximum adsorption for both Cu (II) and Fe (III) was obtained at pH 4.5–5 which were the initial pH of the

solutions. At pH values higher than 6, the change in capacity values was decreased for copper and iron. It is known that pH of the solution determines the state of metal ion species and the surface charge state (Ingle *et al.*, 2015). At much higher pH above 5, hydrolysis of copper ion occurs forming the colloidal complex which was difficult to be adsorbed on the sorbent giving lower removal percentage. Low adsorption percentage removal below pH 5 was expected and can be explained by several factors: (a) repulsion between positive charge of the sorbent and free metal cations, (b) competition between H⁺ and free metal cations for the sorbent active sites, (c) lower formation of complexes with metal ions due to protonation of surface functional groups (Meseldzija *et al.*, 2019).

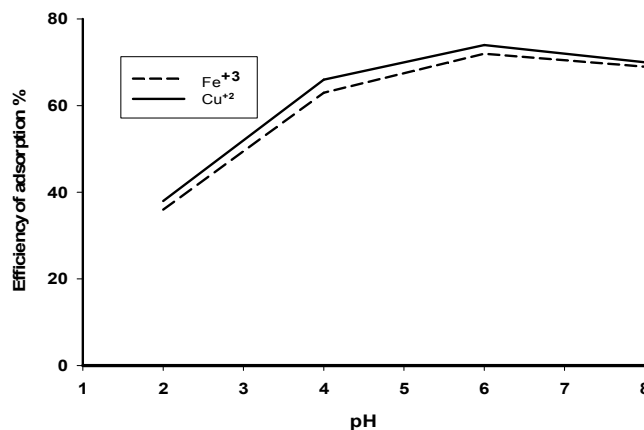


Fig. 2. Effects of pH on Fe⁺³ and Cu⁺² adsorption on potato peel at 30°C, 150 rpm shaking, amount of adsorbent 1g/100ml and the contact time 1h.

Effect of initial concentration

The effect of different initial concentrations of Cu⁺² and Fe⁺³ on the removal efficiency of Cu⁺² and Fe⁺³ is shown in Fig. 3. Results confirmed that the adsorption of Cu⁺² and Fe⁺³ by potato peel was studied at

various copper and iron concentrations in the extent from 50 mg/l to 1000 mg/l. Adsorption efficiencies decreased with the increasing of the iron and copper concentration at constant adsorbent amount 10 g/l. Farai *et al.* (2014) notified that the equilib-

rium curve shows that the overall percent removal of metal from solution decreases with an increase in initial concentration. This may be attributed to lack of sufficient surface area to accommodate much more metal available in the solution. This demonstrate that the adsorbed amount of both heavy metals by the potato peel dependent upon availability of binding sites for Cu^{+2} and Fe^{+3} .

The removal efficiency of studied metals was the highest at 50 mg/l for Cu^{+2} and Fe^{+3} . Similar trend was confirmed by Ali *et al.*, (2014) and Javadian *et al.* (2015). Many studies reported that increasing the initial Cu^{+2} concentration above 500 mg/l

led to decline the percent adsorption of Cu^{+2} indicating saturation of all the binding sites on potato peel, surface beyond a particular concentration and establishment of equilibrium between adsorbate and adsorbent (Malkoc, 2006 and Ozturk *et al.*, 2004). Also observed that extent of compound adsorbed increases with an increase in initial concentration but at the same time removal efficiency (expressed in percentage removal) decreases because of faster saturation of adsorbent surface. Thus, in order to treat water with high metal concentration, dilution of the solution or increase in the biosorbent dosage would be required (Banerjee *et al.*, 2012).

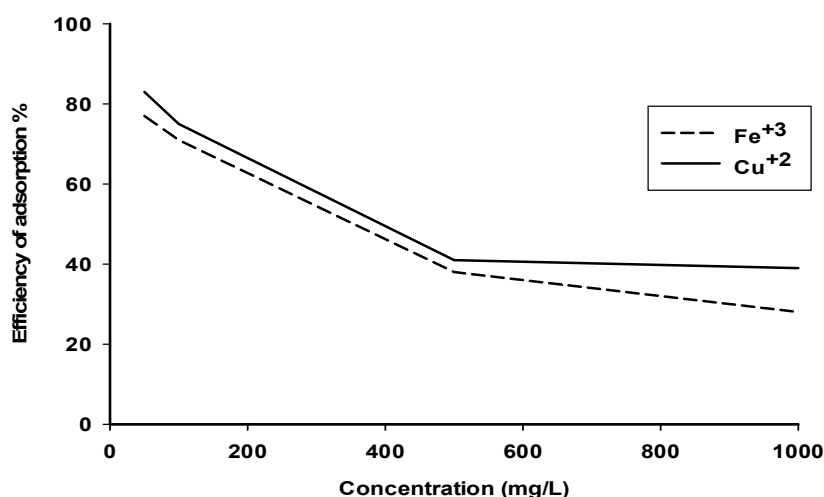


Fig.3. Effects of initial metal concentration on Fe^{+3} and Cu^{+2} adsorption on potato peel, (potato peel concentration was 1g/l, pH =5.0 Contact time was 1h.).

The q_{max} (maximum adsorption capacity) is compared in Table (3 and 4) with the data reported by other researchers for Cu^{+2} and Fe^{+3} biosorption. It can be indicated that the maximum Cu^{+2} sorption value by potato peel was higher than those reported in the literature where the value of q_{max} for Cu^{+2} by potato peel represents 39

mg/g and that indicates the great potential of potato peel as low cost adsorbent material for the removal of Cu^{+2} ions from waste water. In addition, comparing the values of adsorption capacity of Fe^{+3} ions with data reported by other researchers as can be seen, the maximum Fe^{+3} sorption values (28 mg/g) of potato peel was

higher than those obtained in the literature. The comparison shows the great potential of potato peel for removal of ions from waste water, taking the same trend of Fe⁺³. Hala Hegazi, 2013 experimented fly ash and rice husk as adsorbent for Cu⁺² and Fe⁺³ from aqueous solution and other researchers investigated modified many agro byproducts as adsorbent

for Cu⁺² and Fe⁺³ removal from aqueous solutions (Bansode *et al.*, 2003, Saeed *et al.*, 2005, Ozsoy and kumbur, 2006, Ahmed, 2011 and Kondo *et al.*, 2012). Accordingly, it could be concluded that potato peel according to these data represents an excellent potential adsorbent for removal of Cu⁺² and Fe⁺³ from waste water.

Table 3. 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 <i>et al.</i> , 2005 |
| Fly ash | 37.38 | Hala H., 2013 |
| Pecan shells activated carbon | 31.7 | Bansode <i>et al.</i> , 2003 |
| Rice husk | 24.49 | Hala H., 2013 |
| Zeolite | 1.64 | Babel and kurniwan, 2003 |
| Canola | 35.7 | Feizi and Jalali (2015) |
| Potato peel | 39 | Present work |
| Sun flower | 30.3 | Feizi and Jalali (2015) |
| CNTS immobilized by calcium alginate | 79.9 | Li <i>et al.</i> , 2010 |

Table 4. The adsorption capacity of Fe⁺³ on different adsorbents

| Types of adsorbent | q _{max} (mg g ⁻¹) | References |
|-------------------------|--|---------------------------------|
| Wood sawdust | 32.76 | Ahmed, 2011 |
| Green micro | 63.09 | Kondo, <i>et al.</i> , 2012 |
| Nano hydroxyapatite | 12.11 | Kousalya <i>et al.</i> , 2010 |
| Polisher resin | 36.50 | Aboul.Magd <i>et al.</i> , 2016 |
| Modified chitosan heads | 4.88 | Gandhi <i>et al.</i> , 2012 |
| Natural zeolite | 1.11 | Shavandi <i>et al.</i> , 2012 |
| Chitosan(CTS) | 0.97 | Zou <i>et al.</i> , 2011 |
| Attapulgit (Atp) | 9.2 | Zou <i>et al.</i> , 2011 |
| Chitosan(GLA) | 51.55 | Nagah <i>et al.</i> , 2005 |
| Sun flower | 71.4 | Feizi and Jalali (2015) |
| Potato peel | 28 | Present work |
| Rice husk | 68.59 | Hala H., 2013 |
| Chitosan/ Attapulgit | 36.76 | Zou <i>et al.</i> , 2011 |
| Hazelnut hulls | 13.59 | Sheibani <i>et al.</i> , 2012 |
| Canola | 62.5 | Feizi and Jalali (2015) |
| Fly ash | 46.18 | Hala H., 2013 |

Scanning Electronic Microscopy (SEM):

Micro porous structure of potato peel 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 surface structure capable of uptaking heavy metal ions as well as an irregular and porous microstructure of the biosorbent. It was clearly seen that there was a considerable modifi-

cation on morphology of biosorbent after and before heavy metal ions binding. Satish (2015) also explained the surface morphology of potato peel using Scanning Electron Microscope (SEM), after and before adsorption and the corresponding SEM micro

graphs were obtained accelerating voltage of 10.0 kv at 15000x for after and 1500x for before adsorption magnification. At such magnification, the potato peel particles displayed rough areas of within which micro pores were clearly identified.

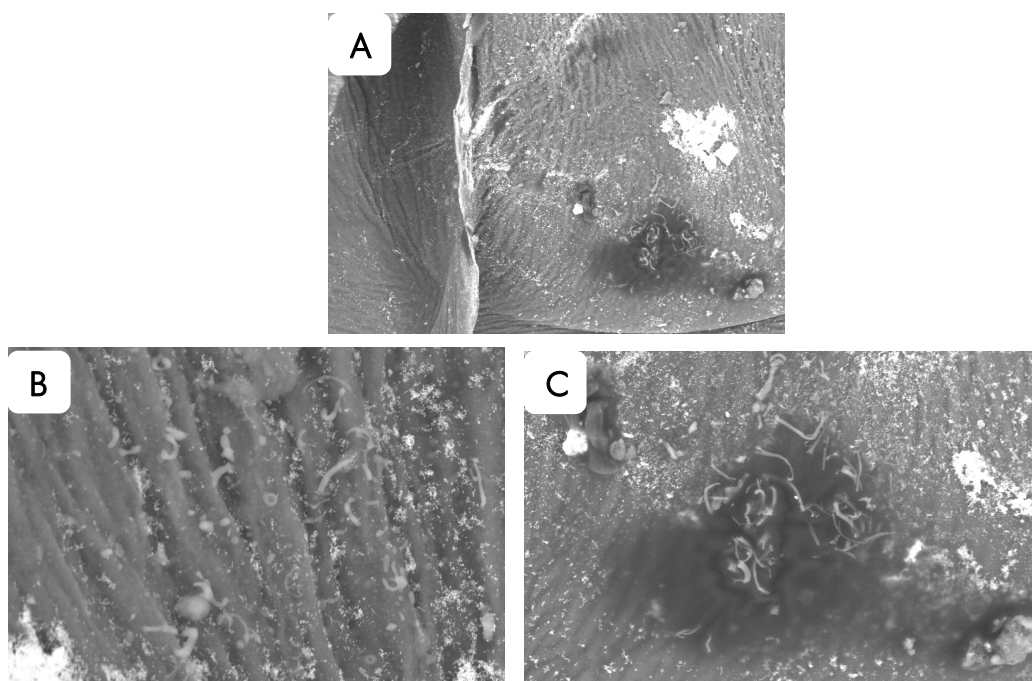


Fig. 4. Scanning Electronic Microscopy (SEM) analyzes of adsorbent particles at 1500x magnification (A) potato peel, (B) potato peel with Cu (II) and (C) potato peel with Fe (III)

Conclusions

The potato peel which are an agricultural waste substance have been converted into a carbonaceous adsorbent material. This product exhibits very good adsorption for copper and ferric (III) from aqueous solution. Adsorption of Cu (II) and Fe (III) by potato peel has been shown to depend on the pH, potato peel dosage and initial concentration. This work clearly indicates the potential of using potato peel as an excellent adsorbent for the removal of Cu (II) from aqueous solutions. One gram of potato peel is found enough to remove 83%

and 77% of the copper (II) and ferric (III) from an aqueous solution.

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ازالة ايونات كلا من النحاس و الحديد من المحلول المائي بالادمصاص باستخدام قشور البطاطس

لمياء محمد مصطفى المغربي

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

الملخص

يهدف البحث الي امكانية استخدام قشور البطاطس لازالة كلا من ايونات النحاس والحديد من المحاليل المائية وذلك بدراسة تاثير كلا من كمية المادة وتركيز العنصر ودرجة الحموضة. قد تبين من النتائج أن ادمصاص العناصر الثقيلة علي المادة المستخدمة زاد زيادة واضحة في مدي درجة حموضة ٥ الي ٦ وظهرت النتائج ان ازالة العناصر الثقيلة المتمثلة في الحديد والنحاس كانت بكفاءة عالية باستخدام اغلفة قشور البطاطس كمادة بيولوجية لها القدرة علي الادمصاص حيث اظهرت النتائج ادمصاصا كبيرا لكلا من النحاس و الحديد. هذا وقد كان اقصي معدل ادمصاص هو ٣٩ و ٢٨ ملليجرام/ جرام لكلا من النحاس و الحديد علي التوالي. هذا ويوصي هذا البحث ان قشور البطاطس تعتبر مادة صديقة للبيئة وذات كفاءة عالية لادمصاص العناصر الثقيلة علاوة علي ذلك فهي رخيصة الثمن.