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Adsorption of heavy metals from polluted water using low cost materials

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ABSTRACT

In this study chitosan and activated carbon (AC) were used as low cost materials for heavy metals removal and they were characterized by SEM, FTIR and X-ray. In the case of batch experiment chitosan and AC give a good removal of Fe, Cu and Zn from aqueous solutions under the effects of sorbent dose, pH, contact time, temperature and initial metal concentration. For application of the removal effect of chitosan and AC on water samples collected from River Nile at Helwan, Hawamdia and El-Kanater El-Khiria cities in greater Cairo, the two sorbents showed excellent removal of the industrial wastewater. Our results show the order of removal of the investigated heavy metals for chitosan were Fe> Pb> Cu> Zn> Mn while for AC were Mn> Cu> Fe> Pb> Zn. So chitosan and AC can be used as a good absorbent materials cheap, effective and nontoxic for heavy metal removal.

INTRODUCTION

The greatest challenge of the modern age is water pollution with inorganic and organic pollutants which poses serious health risks to the human health and wildlife. Many studied have been done for wastewater treatment to make it clean, reusable, and to meet the increasing demands of fresh water. One of the famous strategies for water treatment is adsorption technology. The significant efforts been made over the years to develop highly selective and efficient adsorbent materials. Despite the great achievements, researchers are now focusing on developing the materials that are non-toxic, biocompatible, cost effective and efficient at the same time. Dendritic polymers are hyper branched macromolecules with unique three-dimensional structures decorated with a huge number of reactive end groups. They are relatively cheap, less-toxic, easy to functionalize over other substrates and highly efficient (Sajida, *et al*., 2018). Water quality is the most essential and important resource on the earth which is continuously deteriorating due to contamination with domestic, agricultural and industrial activities which produce thousands of organic, inorganic and biological pollutants, so the need to find low cost adsorbent, environmental friendly, and easy regeneration is increasingly vital with the rapid development of industry (Wang and Zhuang, 2018). Currently, many scientists are focusing on the usage of agricultural wastes and crustacean byproducts as low cost adsorbents to solve the problems of water and environmental pollution (Menya, *et al*., 2018). Activated carbon is suitable for adsorption of chemicals, heavy metals, toxic chemicals, separation of gases,

recovery of solvents, removal of organic pollutants and petrochemicals due to their high micro porosity, surface area, and adsorption capacity (Jyotsna, *et al*., 2005). Chitosan is basic polysaccharide and partially deacetylated polymer of glucosamine obtained from chitin by alkaline deacetylation (Ghannam, *et al*., 2016). In recent years chitosan-based adsorbents have attracted increasing attention in water and wastewater treatment due to its abundance and low price, as well as rich amino and hydroxyl groups. However, there are some drawbacks hindering its practical use, such as low mechanical strength, low solubility in acidic mediums, low adsorption capacity, and lack of selectivity (Wang and Zhuang, 2018). Thus, this study was aimed to prepare chitosan and activated carbon and characterized them by SEM, FTIR and X-ray, then, they were applied for removing of Fe, Cu and Zn from synthetic wastewater. Another application was undertaken on natural pollution sources drain in the River Nile at Helwan, Hawmdia and El-El-Kanater El-Khiria El-Khiria cities during spring 2018. The effects of adsorbent dose, solution pH, contact time and initial metal ion on adsorption efficiency concentration were investigated.

MATERIALS AND METHODS

Preparation of chitosan

Shrimp byproduct including (head, body shells and tails) were obtained from local market and they were extracted according to the method explained by (Toan, 2009). as follows: firstly shrimp byproduct was suspended in 4% HCl at room temperature in the ratio of 1:14 (w/v) for 36 h. Deproteinization of shells was done by treating the demineralized shells with 5 % NaOH at 90°C for 24 h with a solvent to solid ratio of 12:1 (v/w). After the incubation time the shells were washed to neutrality in running tap water and sun dried. The product obtained was chitin which was deacetylatied by employing 70 % NaOH solution with a solid to solvent ratio of 1:14 (w/v) and incubated at room temperature for 72 h and then, the residues were washed with running tap water to neutrality and rinsed with deionized water, then filtered, sun dried and finely grinded to obtained chitosan (Dutta, *et al*., 2004).

Preparation of activated carbon

Rice husk was oven dried at 100ºC overnight then conc H_2SO_4 was added in a weight/volume ratio of 1:1. The resulting black product was washed with water until free from excess acid and dried at 150±5°C. The resulting black mass was kept in a furnace maintained at 400°C for 12 hours for activation. The carbon product obtained was ground well to fine powder which is used for all experiments (Baskaran, *et al*., 2010).

Characterization of the adsorbent

The physicochemical prosperities of chitosan and active carbon which were used as adsorbents in this work are shown in Table (1).

Adsorbates: Metal ions

Analytical grade iron (II) sulfate ($FeSO_4 \cdot 7H_2O$) copper (II) sulfate [$CuSO_4 \cdot 5H_2O$] and zinc (II) sulfate [$ZnSO_4$], reagents from Sigma-Aldrich were used in the experiments. Stock solutions of Fe^{2+}, $Cu^{2+}$and Zn^{2+} (1000 mg/l) were prepared using double distilled water. Metal ion concentrations were determined using Inductively Coupled Plasma Optical Emission Spectroscopy (Varian Liberty II ICP-OES).

Characterization of chitosan

Moisture, protein and ash contents of obtained chitosan were determined according to the AOAC, (2007). Yield was determined according to Mohanasrini-

vasan, *et al*., (2014). Water and fat binding capacity were measured according to Wang and Kinsella (1976).

Degree of deacetylation (DD)

FTIR instrument was used for the determination of DD of the three types of chitosan. The percentage of the acetylated amine group was determined by the following formula:

DD (%) = 100 - [(A1629.85cm^{-1}- A3450.65cm^{-1})/1.33× 100] Struszczyk (1987)

Scanning electron microscopy (SEM) having a magnification range of 5,000 and accelerating voltage 20 kV were used for characterization of prepared chitosan.

X-ray diffraction

X-ray diffraction (XRD) was measured at room temperature by using a Philips diffractometer using Model PW-3710. The patterns were progressed with Ni-filtered copper radiation ($\boldsymbol{\lambda}$= 1.5418˚A) at 30 kV and 10 mA with a scanning speed of 2θ= 5◦/min. The mean crystallites size were calculated using the Debye-Scherrer Eq. (1),

$$\boldsymbol{D = \frac{K\lambda}{\beta \cos\theta}} \qquad \boldsymbol{(1)}$$

Where: K is a constant equal 0.9, $\boldsymbol{\lambda}$ is the wave length of the Cu Kα radiation, β is the half peak width of the diffraction peak in radiant. The different phases were recognized with the help of ASTM powder data files.

FTIR spectroscopy

The Fourier transform infrared (FT-IR) spectra were monitored via a single beam Thermo scientific Nicolet iS10 instrument. The samples were grounded with KBr (1:100) to form tablets, and thus confined into the sample holder in the spectrometer cavity to record the measurements in the 4000-400 cm^{-1} region.

Characterization of activated carbon

Conductivity and pH values were analyzed using instrument CRISON Multimeter MM 40. Moisture and ash contents (%) by mass, bulk density (g/L), specific gravity, water soluble matter, acid soluble matter were determined according to ISI (1989).

Adsorption experiments

Adsorption studies were performed by the batch technique. The pH values of solutions were adjusted by addition of HCl and NaOH. A series of 50 ml conical flasks were used. The flasks were shaken at 25, 30, 35 and 40ºC temperature and the shaking speed was 150 rpm. The adsorption experiments were carried out as follow:
Experiment 1. The effect of adsorbent dose which ranged from 20 to 60 mg/l.
Experiment 2. The effect of initial concentrations which ranged from 5 to 30 mg/l.
Experiment 3. The effect of initial pH ranged from 4 to 9.
Experiment 4. Effect of temperature on the adsorption of ions: The adsorption experiments were conducted at four different temperatures 25, 30, 35 and 40ºC in a thermostat shaker machine.
Experiment 5. The effect of contact time which ranged from 30-360 minutes.

RESULTS AND DISCUSSION

Physical and chemical characterization of chitosan and activated carbon

Moisture, nitrogen, ash, yield, WBC, FBC and DD of the extracted shrimp chitosan recorded 1.70, 8.16, 0.60, 25.70, 1.25, 698 and 87%, respectively. While, pH, conductivity, moisture, ash, bulk density, specific gravity, WSM and ASM of the extracted activated carbon were 6.05, 0.29 (mS/cm), 3.19 (%), 9.90 (%), 0.81 (g/l),

0.92, 1.17 (%) and 0.89 (%), respectively (Table 1). The obtained results agree with those reported by Ghannam, *et al*., (2016).

Table 1: Physical and chemical properties of activated carbon and chitosan

Activated carbon		**Chitosan**	
Properties	**Values**	**Properties**	**%**
pH	6.05	Yield (%)	25.70
Conductivity (mS/cm)	0.29	Moisture (%)	1.70
Moisture content (%)	3.19	Nitrogen (%)	8.16
Ash content (%)	9.90	Ash (%)	0.60
Bulk density (g/L)	0.81	WBC (%)	1.25
Specific gravity	0.92	FBC (%)	698
Water soluble matter (WSM), %	1.17	DD (%)	87
Acid soluble matter (ASM), %	0.89		

Characterization of the adsorbents

Scanning electron micrograph (SEM)

The microstructure SEM images of chitosan showed non-smooth and non-homogenous surface while for the activated carbon the surface was smooth, with few cracks or voids (Figure 1).

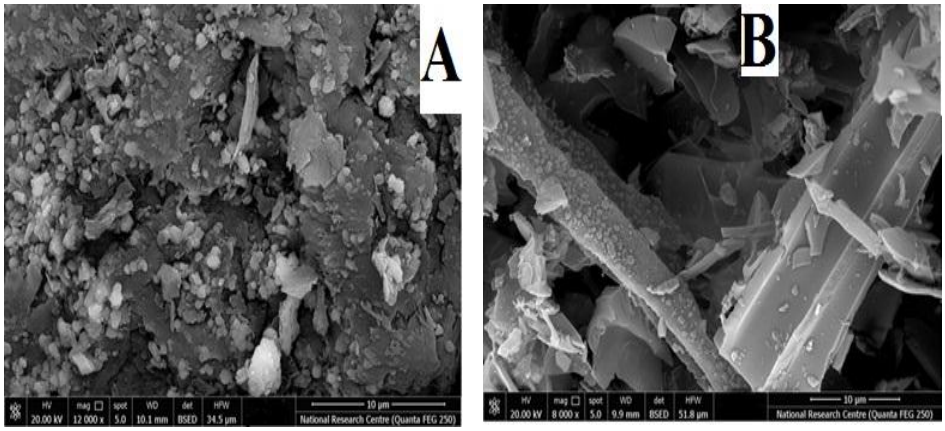

Fig. 1: SEM image of (A) chitosan and (B) activated carbon.

Surface functional group analysis

FTIR analyses for chitosan and activated carbon in order to identify the appearance and disappearance of functional groups were given in Tables (2 and 3) and represented graphically in Figures (2 and 3).

Thus, FTIR spectra of chitosan and activated carbon showed different peaks of different functional groups according to their corresponding wave numbers. The absorption bands at 3410 and 3427 cm^{-1} are assigned to O–H groups which present in phenols, alcohols and carboxylic acids were in the chitosan and activated carbon. Also absorption bands at 2930 and 2921 cm^{-1} indicate C-O stretching in methyl and methylene groups appeared in chitosan and activated carbon. The absorption bands for the adsorbents at 1650 and 1615 cm^{-1} corresponds to C=C stretching of olefins. The band at 1420 cm^{-1} for chitosan and 1422 cm^{-1} for activated carbon is due to C=O stretching mode of the carbonyls, carboxylic acids, and lactones. The absorption bands at 703 and 1047 cm^{-1} for chitosan and activated carbon maybe due to ethers, esters, carbonyl groups, and phenol groups. Finally, the absorption band at 577 cm^{-1} is due to the C-Cl group. The obtained FTIR analysis showed that, the surface of chitosan and activated carbon have acidic functional groups which improves the metal

adsorption such as, alcohol, carboxyl and carbonyl groups and this result agree with those reported by Edwin (2008).

Table 2: Possible assignment of chitosan

Functional class	Band position/cm	Intensity	Assignment
Alcohols	3410	Strong	O–H (H-bonded), usually broad
Carboxylic	2930	Weak	–COO–H (very broad)
Alkenes	2880	Weak	C=C (symmetry reduces intensity)
Aliphatic aldehydes	1650	Strong	C=O (saturated aldehyde)
Aromatics	1420	Strong	C–C (in-ring)
Thiocarbonyl	1200	Strong	C=S
Esters	703	Strong	S–OR

Table 3: Possible assignment of activated carbon

Functional class	Band position/cm	Intensity	Assignment
Alcohols	3427	Strong	O–H (H-bonded), usually broad
Carboxylic	2921	Strong	–COO–H (very broad)
Aliphatic aldehyde	1651	Variable	C=C (symmetry reduces intensity)
Aromatics	1422	Weak	C–C (in-ring)
Esters	1047	Strong	S–OR
Alkyl halide	577	Weak	C–Cl

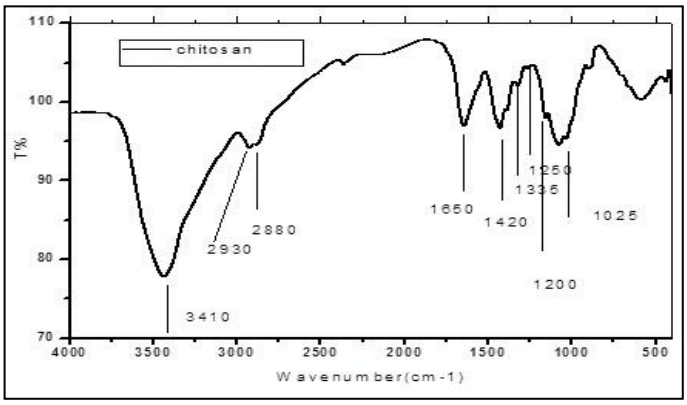

Fig. 2: FTIR spectrum of chitosan

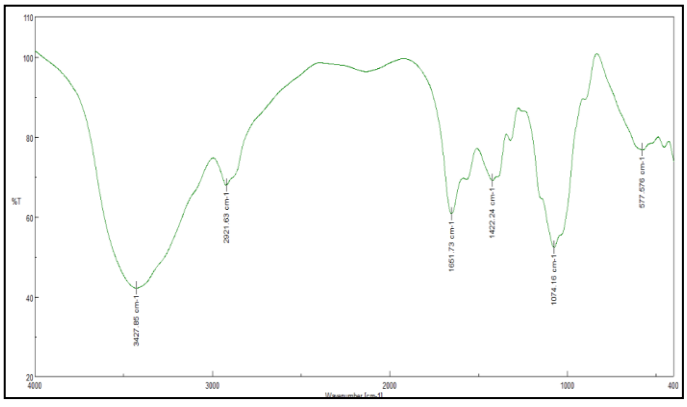

Fig. 3: FTIR spectrum of activated carbon

XRD analysis

Figures (4 and 5) illustrates the X-ray diffraction profile of the extracted chitosan and activated carbon. Chitosan shows a sharp peaks at 2θ=25.3°, 27.7°,

36.1°, 39.2°, 41.1°, 44.1°, 54.5°, 56.7°, 62.9°, 64.1°,69° and 70° while activated carbon exhibit very broad diffraction peaks and the absence of a sharp peak reveals a predominantly amorphous structure (Wang and Lu, 1997). There are two broad diffraction peaks at 2θ = 26.5° and 46.1° in spectrum. The appearance of the peak at around 24° signifies an increasing regularity of crystalline structure (Kasaoka, *et al*., 1989).

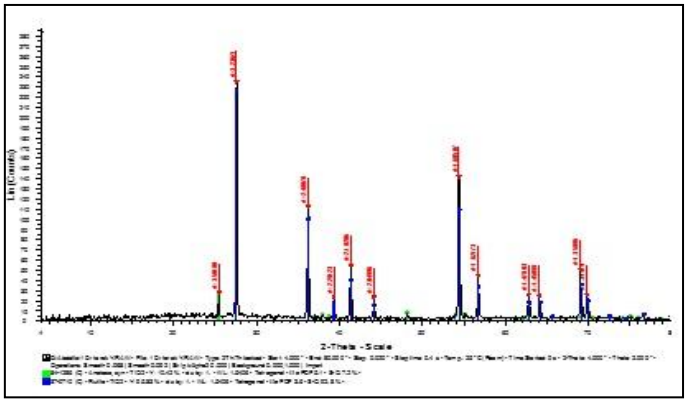

Fig. 4: X-ray of chitosan

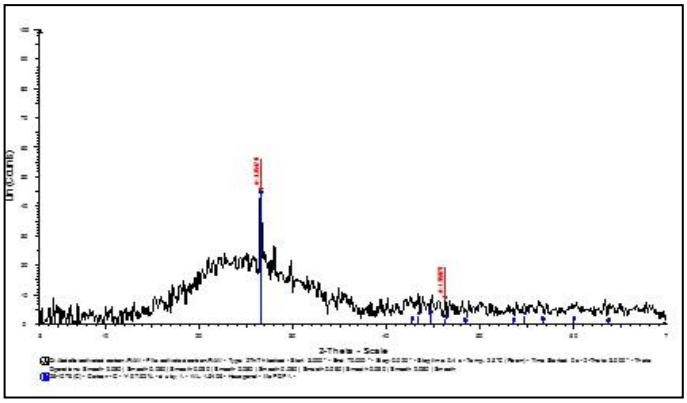

Fig. 5: X-ray of activated carbon

Effect of sorbent dose

From (Fig. 6) the effect of sorbent dose were studied and the values were changed from 20 to 60 mg/l. In the case of chitosan the highest removal was 88% for Zn followed by 85% for Fe and finally was 84% for Cu at sorbent dose 60 mg/l. While for AC the maximum removal for Zn was 86% and for Fe and Cu the percent were similar 80%. The chitosan and AC follow the trend that by increasing the sorbent dose the efficiency also increased.

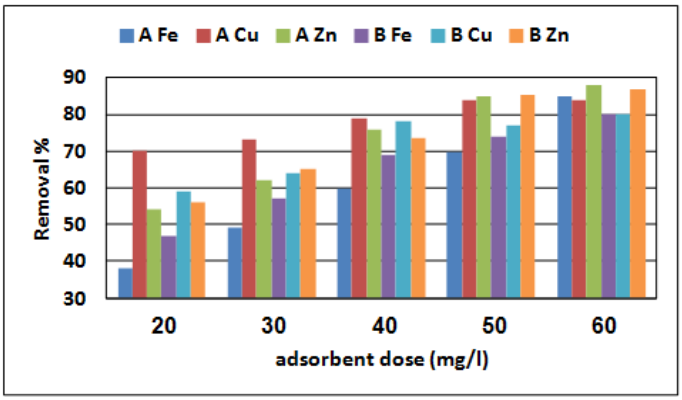

Fig. 6: Effect of adsorbent dose on removal percent of heavy metals from wastewater using (A: chitosan) and (B: activated carbon).

Effect of pH

The effect of pH on the removal efficiency of heavy metal from 4 to 9 is shown in (Fig. 7). The results revealed that, the removal efficiency in chitosan increased by increasing pH for Fe and Zn with the maximum removal rate were 65% and 72% at (pH=9). There was an exception in Cu the maximum removal was75% at pH=5. For AC the same trend were found, the maximum removal were 55% and 75% for Fe and Zn at pH=9 but for Cu was 80% at pH =4. The results showed that for Fe and Zn for chitosan and AC the efficiency increased by increasing pH while Cu give highest efficiency at low pH in the acid medium.

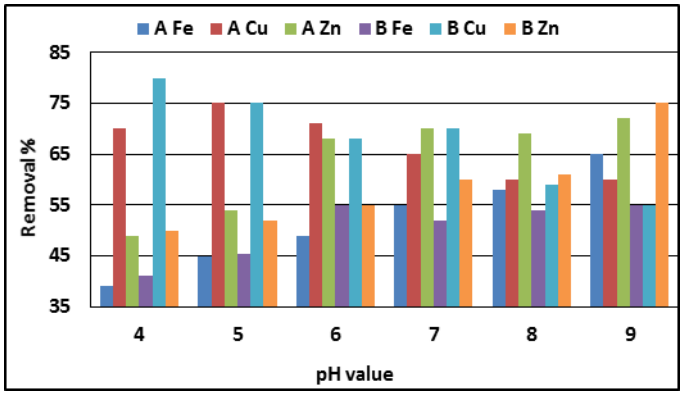

Fig. 7: Effect of pH on removal percent of heavy metals from wastewater using (A: chitosan) and (B: activated carbon).

Effect of contact time

In the case of contact time (Fig. 8) the time ranged from 30 to 360 minute.

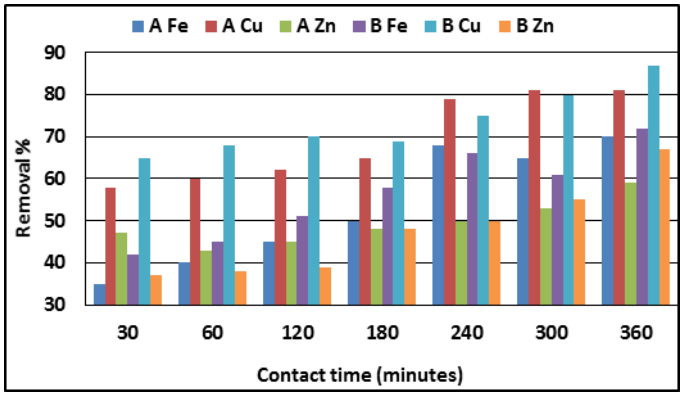

Fig. 8: Effect of contact time on removal percent of heavy metals from wastewater using (A: chitosan) and (B: activated carbon).

For chitosan the results indicate that, the removal efficiency were 70%, 81% and 59% for Fe, Cu and Zn respectively. The highest value was for Cu and the lowest for Zn. In A.C the removal efficiency for Fe, Cu and Zn were 72%, 87% and 55% respectively, so the lowest efficiency was for Zn and the highest efficiency was for Cu. All the results can be concluded as by increasing the contact time the removal efficiency increased.

Effect of temperature

As seen in (Fig. 9) the effect of temperature on the removal of Fe, Cu and Zn by chitosan were 82%, 80% and 65% respectively. Also for Chitosan as the

temperature increased the efficiency decreased except for Fe. In AC Fe, Cu and Zn showed the removal efficiency 73%, 70% and 58% respectively, for AC all the metals follow the same trend that, the efficiency increased by decreasing temperature.

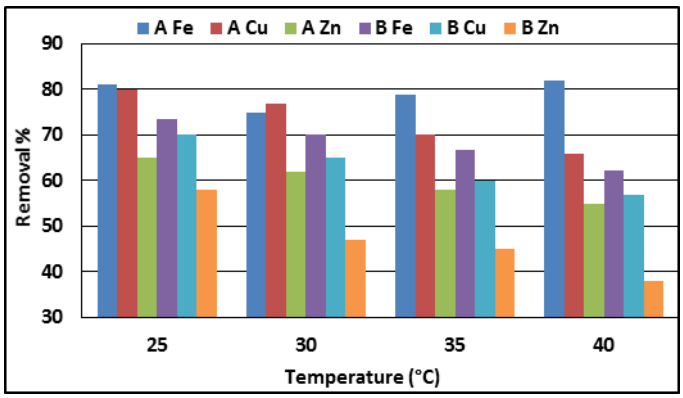

Fig. 9: Effect of temperature on removal percent of heavy metals from wastewater using (A: chitosan) and (B: activated carbon).

Effect of initial metal concentration

In the case of study the effect of initial metal concentration (Fig. 10). The results showed that, the maximum removal efficiency for Fe was 58% at 5 mg/l and for Cu and Zn were 68% and 69% at 10 mg/l for chitosan. Also, for AC the maximum removal efficiency were 74% and 70% for Fe and Cu at 5 mg/l while for Zn was 78% at 10 mg/l. As showed the efficiency decreased as the concentration increased.

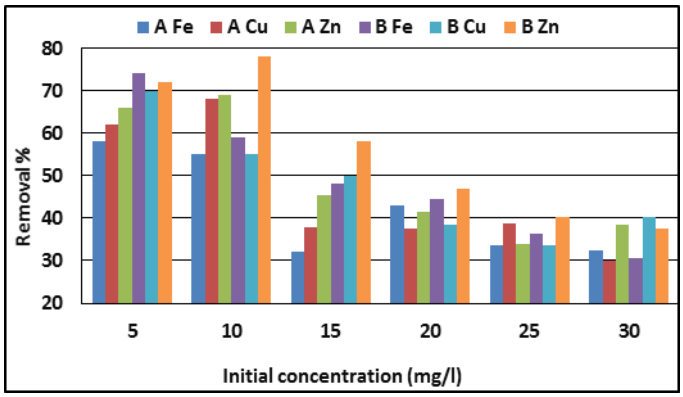

Fig. 10: Effect of initial concentration on removal percent of heavy metals from wastewater using (A: chitosan) and (B: activated carbon).

Application study

Table (4) illustrate the effect of chitosan and active carbon on heavy metals removal in the polluted water collected from River Nile. For chitosan the highest removal was 93% for Fe at El-Kanater El-Khiria followed by Pb 92% at Helwan then 86% for Cu at El-Kanater El-Khiria and 75% for Zn at Helwan, finally 57% for Mn at Helwan. So the removal efficiency of heavy metals from the polluted water using chitosan were in following order: Fe> Pb> Cu> Zn> Mn. On the other hand AC give highest removal efficiency 95.8% for Mn at Helwan then 95.1 % for Cu at El-Kanater El-Khiria and 87% for Fe at El-Kanater El-Khiria followed by 84% for Pb at Helwan lastly 83% for Zn a Helwan. Also the effect of AC on heavy metal removal follow the order: Mn> Cu> Fe> Pb> Zn.

Table 4. Metal removal efficiency of heavy metals from water samples collected from River Nile at Greater Cairo using chitosan and activate carbon

Metals	Polluted sources	Chitosan			Activated carbon		
		Co	*Cf*	*R %*	*Co*	*Cf*	*R %*
Fe	Helwan	0.371	0.025	93.261	0.371	0.050	86.523
	Hawmdia	0.282	0.023	91.844	0.282	0.040	85.816
	El-Kanater El-Khiria	0.247	0.015	93.927	0.247	0.030	87.854
Mn	Helwan	0.241	0.102	57.676	0.241	0.010	95.851
	Hawmdia	0.211	0.111	47.393	0.211	0.020	90.521
	El-Kanater El-Khiria	0.185	0.106	42.703	0.185	0.020	89.189
Cu	Helwan	0.132	0.025	81.061	0.132	0.011	91.667
	Hawmdia	0.115	0.022	80.870	0.115	0.015	86.957
	El-Kanater El-Khiria	0.145	0.020	86.207	0.145	0.007	95.172
Zn	Helwan	0.736	0.180	75.543	0.736	0.120	83.696
	Hawmdia	0.685	0.175	74.453	0.685	0.130	81.022
	El-Kanater El-Khiria	0.502	0.170	66.135	0.502	0.101	79.880
Pb	Helwan	0.767	0.055	92.829	0.767	0.120	84.355
	Hawmdia	0.490	0.045	90.816	0.490	0.090	81.633
	El-Kanater El-Khiria	0.010	0.001	90.000	0.010	0.002	80.000

CONCLUSION

River Nile water pollution by heavy metals in Egypt is a very serious problem because of their dangerous effect on human. This study give solution in heavy metals removal using materials that can pollute our environment. Chitosan prepared from wastes of shrimp and activated carbon from rice husk were used for removal of heavy metal. The present results give an indication for good removal effect of the two adsorbents.

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