Usage of crayfish chitosan composite modified film, prepared from exoskeleton of *Procambarus clarkii*, in treatment of water copper toxicity

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ABSTRACT:

Freshwater crayfish species are considered to be the largest and the most valuable invertebrate of all inland water, so it can be used as an environmental indicator. This study aimed to use an extract from its exoskeleton in treatment of water copper toxicity, the most abundant heavy metal along aquatic habitats. Three different composite films were prepared from the exoskeleton of *Procambarus clarkii*, and used for wastewater remediation. In this study, film efficiency towards copper ions was determined and showed that the maximum removal was achieved by the third one which is incorporated by a Porogen substance, and increased with increasing contact time until reaching equilibrium where removal rate remains constant. The increase in temperature (25-55°C), reduces the efficiency of the all three films in removing copper ions, the best temperature value for removing copper ions for all three films, was 25°C. The thermodynamics and kinetics was studied for the third composite modified film, the adsorption process was exothermic and the kinetic model, pseudo second order is fitted to it. Adsorptive sites energy of the modified composite film was studied by applying two isothermal models; Langmuir and Freundlich models, Langmuir model was fitted to it.

KEYWORDS: Water, Remediation, Chitosan, Crayfish, *Procambarus clarkii*

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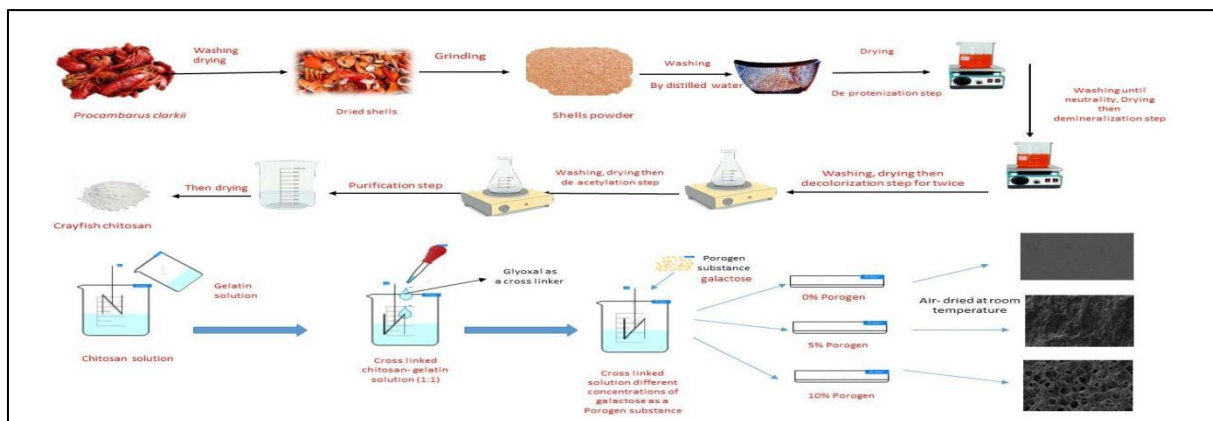
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1- INTRODUCTION:

Water is a vital source of life, but it is under threat from pollution generated by industrial, agricultural, and domestic wastes (Tscheikner-Gratl *et al.*, 2019). Heavy metals are a big problem because it is toxic and tends to accumulate in the organs of the body so it may pose a risk to human health (Vilizzi and Taken, 2016). Copper is one of these heavy metals that may be found in wastewater from a variety of industries, including metal cleaning and plating baths, refineries, paper and pulp, fertilizers, and wood preservatives (Kalavathy *et al.*, 2005). Copper is an indispensable microelement that functions as a cofactor in a variety of enzymes, including oxidases, oxygenase, and others, it is toxic to living organisms at high concentrations (Acemioglu and Alma, 2001). It catalyzes the synthesis of highly reactive oxygen species, resulting in lipid peroxidation and a shortage of the reduced form of glutathione, as well as an increase in methemoglobin concentration (Hu *et al.*, 1990). Cu^{2+} also catalyzes the creation of hydroxyl free radicals, which causes chemical modification of proteins, structural changes in proteins, and oxidative damage to surrounding tissues (Bush, 2000). There are several methods for removing heavy metals from water, including ion exchange, reverse osmosis, nanofiltration, precipitation, coagulation/co-precipitation, electro dialysis, flotation, extraction, electrolysis, and adsorption (Kottaichamy *et al.*, 2020a, b). Adsorption is one of the most often employed removal technologies owing to its cheap operating costs and the possibility of adsorbent renewal (Malik *et al.*, 2017). Biodegradable adsorbents produced from natural precursors are being intensively investigated for viable wastewater treatment, potentially replacing traditional materials.

Green renewable adsorbents made from polysaccharide-based biopolymers (e.g. cellulose, chitin, and chitosan) and their derivatives, are extremely important in the field of heavy metal ion absorption (Acar et al., 2006). Chitosan Polymer is non-toxic, biodegradable and biocompatible (Aranaz *et al.*, 2009; Younes *et al.*, 2016). It is similar to plant fiber, cellulose. However, it contains amine groups instead of the hydroxyl groups present in cellulose. chitosan has been used commercially due to its unique properties including biological activity, process ability, absorbency, film making ability and complexity (Rout, 2001). Chitosan is applied to wastewater treatment in the current industrial sector because it is partially positively charged and binds to metal ions (Díaz-Rojas *et al.*, 2006; Muzzarelli and Muzzarelli, 2005). Chitosan is a deacetylation product of chitin (poly-N-acetyl-D-glucosamine), which is recovered from insect exoskeletons and crustacean shells, resulting in a linear polysaccharide composed of -(1-4)-linked D-glucosamine units (Liu *et al.*, 2002). Chitosan-based sorbents have comparatively high sorption capacities and kinetics for heavy metals due to their high nitrogen content and porosity (Keong and Halim, 2009). However, chitosan's utilization is unsatisfactory due to its poor solubility, mechanical strength, elasticity, and pKa value (about 6.3–6.4), so we can blend it with other natural polymers.

Gelatin is a water-soluble biopolymer that is formed as a byproduct of the decomposition of the water-insoluble protein collagen and has the potential to remove heavy metals from drinking water (Chen *et al.*, 2014). Gelatin is a useful bio adsorbent in wastewater treatment due to its non-toxicity, biodegradability, low cost, and simple availability, as well as the presence of several functional groups (–OH, –NH, and –COOH)

that act as binding sites via polar or ionic interactions. Nonetheless, the non-covalent linkages within the 3D gelatin network are easily broken in water in a mild temperature range (30–35°C), resulting in the physical network being destroyed. These constraints might be avoided by forming stable covalent amide connections between the gelatin backbone's carboxyl groups and amino groups via crosslinking.

In this study, we extracted chitosan from *Procambarus clarkii* exoskeletons, and then cross-linked it with another natural polymer (gelatin) to improve the limitations of each one and to increase the number of metal binding sites. Also in order to increase water penetration of the film, we used a Porogen substance (galactose) to increase the number of pores on the film surface and consequently increase adsorption metal ion capacity via chelation or ion exchange mechanism.

2- MATERIALS AND METHODS:

Chitosan recovery from *Procambarus clarkii* exoskeleton

Samples of crayfish were collected from Fayoum Governorate, Egypt. The collected samples were carried alive to the laboratory, washed very well with tap water then distilled water to remove any impurities, then dissected and exoskeletons were collected.

Exoskeleton was deproteinized using sodium hydroxide solution (3.5%) with regular stirring (1:10 w/v) at 70°C for 2 hours, it was then filtered, washed with distilled water for 1 hour and dried in the oven (No and Meyers, 1989). The protein-depleted crayfish exoskeleton was treated with IN HCL for 1 hour (1:20 w/v), washed with distilled water for 1 hour (No and Meyers, 1989), and then dried in the oven. The dried chitin was decolorized with acetone for 30 minutes, dried at room temperature for 2 hours, and then bleached with hydrogen peroxide at a ratio of 1:20 (w/v) at room temperature for 1 hour. The samples were washed with tap water and dried at 250°C for 4 -5 hours until the exoskeleton was crispy (No and Meyers, 1989), to remove acetyl groups of chitin, the samples was immersed in concentrated sodium hydroxide (50%) at a ratio of 1:20 (w/v) at 100°C for 2 hours, then left at room temperature for 2 days. Samples neutralized by water and then dried overnight at 70°C. The extracted chitosan was purified by dissolving it in acetic acid (3%) then precipitate it again by adding NaOH (1M) drop by drop with regular stirring, then the precipitated was neutralized by washing with distilled water several times then vacuum dried.

2. Physicochemical characterization of crayfish chitosan and a commercial chitosan

- **Moisture content**:

Measurement of chitosan weight before and after drying (Black, 1965).

$$Moisture\ content\ \% = \left[\frac{weight\ before\ drying - weight\ after\ drying}{weight\ before\ drying}\right] \times 100$$

- **Ash percent:**

Chitosan (2.0 g) was heated at 600 °C for 16 hours in a muffle, and then the residue (g) was measured according to Aoac (1990).

$$Ash\ \% = \left[\frac{weight\ of\ residue}{initial\ weight\ of\ sample}\right] \times 100$$

- **Determination of deacetylation degree value of extracted crayfish chitosan:**

Deacetylation degree value of crayfish chitosan was investigated from analytical method, Fourier transform infrared Spectroscopy (FTIR) instrument (Mattson

Satellite FTIR) in which chitosan DD was measured according to the following reference equation (Islam *et al.*, 2011).

$$DA\% = \left[\left(\frac{A_{1320}}{A_{1420}}\right) - 0.3822\right]/0.03133$$

DA represent degree of acetylation, DD %= 100 - DA, DD represents the degree of de acetylation, A_{1320} represent absorbance at wavelength number 1320 cm^{-1} as a measure

of the amide group, while A_{1420} represents absorbance at wavelength 1420 cm^{-1} as a measure of the amine group.

- **Solubility:**

This was done by dissolving 1.00 g of chitosan sample in 10.00 ml of 1% acetic acid (pH = 4), continuously stirring for one hour with a magnetic stirrer. The solution was submerged in a boiling water bath (10 minutes) and left at 25^{0}C to be cooled. After a centrifugation process, the insoluble

particles are separated for ten minutes at 13,000 rpm, then washed by dist. water (25ml) and centrifuged once again at 10,000 rpm. The supernatant was discarded, and the undissolved particles were dried in a vacuum oven for 24 hours at 60°C.

$$Solubility\% = \left[\frac{initial\ weight\ of\ chitosan - dried\ insoluble\ weight\ of\ chitosan}{initial\ weight\ of\ chitosan}\right] \times 100$$

Preparation of crayfish chitosan composite films

Chitosan solution was prepared by dissolving 2 g in 100 ml acetic acid (1%) with continuous stirring for 30 minutes with magnetic stirrer and heated at 60 ^{0}C, then leaved at room temperature for cooling then filtered to remove any insoluble particles. Also gelatin solution was prepared by dissolving 2 g of gelatin in 100 ml acetic acid (70%) with continuous stirring for 20 minutes by using a magnetic stirrer. Then 50 ml from each solution were mixed together (1:1) to form a blend solution, then a cross-linker (glyoxal), approximately 5 ml, was added drop wise to the blended solution with a continuous stirring for 30 minutes by using a magnetic stirrer, then leaved overnight to get a homogenous solution and get more ripening blended solution. Finally, a Porogen substance (galactose) with different concentrations (0.5-10%) with a continuous stirring for 24 hrs. Then pour 50 ml of each blended solution into a polystyrene petri dish,

then air dried for 48 hrs. All three films were peeled off and kept under evacuated desiccators until use. Films were characterized by using scanning electron microscope.

Preparation of stock solution of copper ion:

Solutions of copper ions were prepared at different concentrations in the range 10 - 120 mg/l, which indicates the known initial concentrations of metal ions.

Adsorption capacity study:

This study was conducted to determine the adsorption capacity of our films for specific copper ion at different pH, different times and temperatures with different metal ion concentrations in the range 10 - 120 mg/l. The concentrations were measured by atomic absorbance spectroscopy (SHIMADZU AA-7000). Metal absorption capacity is determined by the following formula.

$$Removal~\% = \left[\frac{initial~metal~ion~concentration - final~metal~ion~concentration}{initial~metal~ion~concentration}\right] \times 100$$

Thermodynamic study for metal ion adsorption on the third composite film:

Three parameters were calculated for the adsorption behavior of metal ion on the composite film at the studied temperature values (Lin *et al.*, 2015; Hasan *et al.*, 2016), free energy parameter (ΔG^0), enthalpy parameter (ΔH^0), and entropy parameter (ΔS^0), were calculated for copper ion adsorption on it as shown in table (6).

The following equation was used to measure entropy and enthalpy values from the slope and intercept of plotting lnK vs 1/T

$lnK_{eq} = - \Delta H^0 / RT + \Delta S^0 / R$

T represents temperature (K)

K_{eq} is the constant of equilibrium

R is universal gas constant (8.314 J/mol k)

From the following equation, free energy can be detected:

$\Delta G^0 = \Delta H^0 - T \Delta S^0$

Isothermal models for the composite film potency:

Adsorption isotherms represent equilibrium data of the adsorption process, and this very important study shows the effectiveness of our adsorbent material under different states. In this study, we used two models which are, Langmuir, Freundlich isotherms.

The Langmuir, Freundlich equations, are the following:

$C_e / q_e = 1/ K_L Q_0 + C_e / Q_0$, Langmuir equation, this model presumes that the adsorption process happens at equivalent energy adsorption sites on a homogeneous surface.

Where C_e represents equilibrium metal concentration (mg/l), q_e represents equilibrium adsorbed amount of our study metal (mg/g), K_L represents constant of Langmuir equilibrium (L mg^{-1}), Q_0 represents maximum adsorption capacity (mg.g^{-1})

$Log~(q_e) = Log(K_f) + 1/n~Log~(C_e)$

The previous equation reflects the Freundlich model, which assumes that the adsorbent material surface is heterogeneous and has different energy adsorbent sites.

Kinetic studies of adsorption process between the metal ion and the composite film:

This study is very important in wastewater treatment in which it describes the mechanism of the reaction between adsorbate and adsorbent material. There are two mechanisms of this model.

$Log~(q_e - q_t) = Log~q_e - (K_1/ 2.303)~t$, this represents a pseudo – first order model according to Ho and Mckay (1999a). The adsorption rate can be measured by plotting $Log~(q_e - q_t)$ vs t.

K_1 (min^{-1}) represents the constant rate of the pseudo-first-order model.

q_t (mg/g) represents adsorption amount at time t (min.)

q_e (mg/g) represents adsorption amount at equilibrium

$T/ q_t = (1 / K_2 q_e^2) + t / q_e$, this represents pseudo- second order model according to Ho and McKay, (1999b) Where K_2 (min^{-1}) represents the constant rate of the pseudo- second order model.

Statistical analysis

Data are presented as mean ± standard error and one way of variance (ANOVA) was used to analyze the data.

3- RESULTS AND DISCUSSION:

Environmental pollution has been one of human's most pressing issues for decades, as it has a negative effect on human wellbeing and the whole of organisms. Heavy metal contamination is one of the most dangerous types of pollution because of its accumulation in biological tissues and failure to excrete, and it has resulted in several severe health issues around the world. Water is one of the basic factors for human life and all living creatures on the earth surface, so it is important to be treated. In our study, a green renewable adsorbent polymer, chitosan, was extracted from the exoskeleton of red swamp crayfish, *Procambarus clarkii*. It has been found that the extracted chitosan has good physicochemical properties compared to the commercial one, as it has a low ash and moisture content and a high solubility degree compared to the commercial one (table 1). Ash parameter for our sample is 0.2 % which indicates that it has a high quality grade because this parameter has a great effect on solubility and viscosity of chitosan. As ash content decreases, the solubility increases and viscosity decreases, this is in agreement with No and Meyers (1995). Depending on visual observation, our chitosan is white in agreement with No and Meyers (1995) which stated that chitosan color ranged between pale yellow and white color. Characteristic spectral bands of the extracted chitosan **(table 2),** were recognized by FTIR, Fourier Transform infrared spectra, as -OH band (3566 cm^{-1}), -CONHR band (2870 cm^{-1}), O=C=O (2349 cm^{-1}), amide band (1550 cm^{-1}), amine band NH_2 band (1488 cm^{-1}), aromatic band C-O (1310 cm^{-1}) while C-O-C stretching band (1064 cm^{-1}) and glyosidic linkage of amides (890 cm^{-1}). Crayfish chitosan DD was measured according to the following baseline equation (Islam *et al.*, 2011), [DA%= ({A_{1320}/A_{1420}} - 0.3822) / 0.03133], where DA represents degree of acetylation. and was found to be 94%, DD%=100 – DA, DD represents the degree of deacetylation., A_{1320} represents absorbance at wavenumber 1320 cm^{-1} as a measure of the amide group, while A_{1420} represents absorbance at wavenumber 1420 cm^{-1} as a measure of the amine group.

Chitosan is a deacetylated product of chitin. Owing to its hydrophilicity, biocompatibility, biodegradability and non-toxicity, and the presence of reactive amino (–NH_2) and hydroxyl (–OH) groups on its backbone, chitosan has been widely recommended for the recovery of toxic heavy metal ions from wastewater (Sami El-banna *et al.*, 2019; Akakuru *et al.*, 2018). However, due to its poor solubility, poor mechanical strength, low elasticity and pKa value (about 6.3–6.4), the application of chitosan is unsatisfactory (Matica *et al.*, 2017). Gelatin is a water-soluble biopolymer which is obtained as a degradation product of water-insoluble protein collagen and has the ability to remove heavy metals from drinking water (Lone *et al.*, 2019). The distinctive advantages of nontoxicity, biodegradability, low cost and easy availability, and the presence of various functional groups (–OH, –NH_2, and –COOH) that act as binding sites via polar or ionic interactions have made gelatin an effective bioadsorbent in wastewater treatment. Nonetheless, the non-covalent associations within the 3D gelatin network are easily broken in water over a mild temperature range (30–35°C), consequently destroying the physical network. Such limitations could be overcome by establishing stable covalent amide bonds between carboxyl groups and amino groups of the gelatin backbone, via crosslinking. Gelatin and

chitosan are among the promising biodegradable adsorbent materials applied for efficient heavy metal removal from drinking water (Rigueto *et al.*, 2021). a cross-linked gelatin chitosan blend would be an ideal soft material to address both the limitations of low mechanical stability and actuation repeatability (Dhand *et al.*, 2021). This blend increases the water uptake because gelatin is more hydrophilic than chitosan, increasing the water content of the film will increase the film permeability to oxygen molecules (Xin-Yuan and Tian-Wei, 2004). Also adding gelatin to chitosan film improves strength and mechanical properties of chitosan, chitosan gelatin film is more flexible and homogenous than chitosan film (Xin-Yuan and Tian-Wei 2004). Two polymers show an increased number of binding sites for metal ions (Lone *et al.*, 2019). Our cross linked blended film showed a homogenous surface with no pores by scanning electron microscope (fig. 3), so in order to increase permeability of water through our film and increase its adsorption capacity by generating pores on our thin film by using a Porogen substance (galactose). We prepared three blended films, the first blend (1:1) with no modification while the two others were treated with different concentrations of the Porogen (5% and 10 % respectively). Obtained data revealed that the removal efficiency of our three films depend greatly on pH variation (table 3). The percentage of copper ion removal increased to a maximum point then began to decrease with pH variation by all three films (fig. 4), but the maximum removal happened by the third one that has many pores on its surface (fig. 3). Removal efficiency increased with increasing contact time till reaching an equilibrium state (table 4) at which the removal percentage remains constant at all the three films (fig. 5), this in agreement with

Soliman and Moustafa (2020). The third one has a higher adsorption capacity than the others. From data, the best temperature value for copper ion removal by the three films, was 25 ^{0}C (table 5, fig. 6) and this confirm that the removal efficiency was greater at low temperatures meaning that the adsorption process is physical in nature and exothermic, in agreement with Rigueto *et al.* (2021). Depending on the obtained results, the adsorption capacity of the third modified prepared film was higher than the others, so we applied the thermodynamic, isothermal and kinetic studies on the third one. ΔG^0 (change in free energy) is negative at all temperatures (table 6) shows that the copper adsorption process is spontaneous. As a result, it's safe to assume that the reaction is spontaneous. As the ΔG^0 ranges from -0.01 to -0.003 kJ/mol, the adsorption process is predominantly a physical adsorption process and this is in agreement with Cui *et al.* (2015). The negative value of ΔH^0 (change in adsorption heat) for the removal of copper confirms that the adsorption process was exothermic in nature. The kinetics of adsorption were studied (table 10) for a contact time ranging from (30 - 240 min). The results were fitted to the pseudo first order (fig. 9) and pseudo second order (fig. 10) kinetic model. The R^2 value is higher than the R^1 value indicating that the results show better acceptance to pseudo-second order models, this in agreement with Okasha *et al.* (2019). Hence, the copper adsorption belongs to pseudo-second order. Two isothermal models were fitted to our experimental adsorption data, Langmuir and Freundlich isotherm models (tables 7, 8, 9). The data showed that the Langmuir model (fig. 7) is more fittable than the Freundlich model (fig. 8) to our film, indicating that all adsorption sites have the same energy potency. One could conclude that the

chitosan prepared from the exoskeleton of *Procambarus clarkii*, can be used in preparing a composite film to remove metal ions from wastewater resources especially copper ions in the present study and its efficiency is highest when treated with a Porogen substance.

Table 1. Physicochemical properties of extracted crayfish chitosan and commercial chitosan

parameters	Extracted crayfish chitosan	Commercial chitosan	F - value
Ash content	0.2 ± 0.01***	0.6 ± 0.01***	63.6 ***
Moisture content	0.3 ± 0.01***	0.05 ± 0.01***	242****
Solubility %	75 ± 0.01***	65 ± 0.001***	333***
DD (%)	94 ± 1.1***	75 ± 0.29***	203.1***

- Data are represented as means $\pm$ SE, *** Highly significant $P<0.001$.

Table 2. Comparison of FTIR characteristic bands for extracted crayfish chitosan and commercial chitosan spectral bands.

Functional group	Functional group range	Extracted crayfish chitosan	Commercial chitosan
OH group	3400-3650	3566	3420
CONHR for polymers	2868-2919	2870	2870
Carbon dioxide O=C=O	2349	2349	1645
amide I	1550-1650	1550	1555
amino gp.	1450-1560	1488	1375
aromatic band C-O	1250-1310	1310	1300
C-O-C stretching band	1060-1124	1064	1030
glyosidic linkage of amides	890-900	890	898

C_0 represent initial concentration of metal ion was 50 mg/l, C_i represent concentration after treatment with the modified film, % removal = $((C_0 - C_i) / C_0) \times 100$

Table 3. Effect of time variation parameter on adsorption capacity of three prepared composite films towards copper ion

T_c hrs.	C_i Film 1	C_i Film 2	C_i Film 3	% removal Film 1	% removal Film 2	% removal Film 3
0.5	48.5	47.5	45	3	5	10
1	47	45	40	6	10	20
1.5	45.5	42.5	35	9	15	30
2	44	40	30	12	20	40
2.5	42.5	37.5	25	15	25	50
3	41	35	20	18	30	60
3.5	39.5	32.5	15	21	35	70
4	38	30	15	24	40	70

C_0 represent initial concentration of metal ion was 50 mg/l, C_i represent concentration after treatment with the modified film, % removal = $((C_0 - C_i) / C_0) \times 100$

Table 4. Effect of temperature variation parameter on adsorption capacity of the three prepared films towards copper ion

T_c	C_i film 1	C_i film 2	C_i film 3	% removal film 1	% removal film 2	% removal film 3
25	38	30	15	24	40	70
50	42.5	32.5	17.5	15	35	65
55	47.5	37.5	22.5	5	25	55

C_0 represent initial concentration of metal ion was 50 mg/l, C_i represent concentration after treatment with the modified film, % removal = $((C_0 - C_i) /\ C_0) \times 100$, T_c represent temperature by Celsius degree

Table 5. Thermodynamic parameters of copper adsorption on third modified composite film

$T\ ^0c$	$T\ (K)$	K	$Ln\ K$	$1/T$	ΔG^0	ΔH^0	ΔS^0
25	298	2.30	0.83	0.00341	-0.01	-	2.075
50	323	1.90	0.64	0.00309	-0.005	0.0075	
55	328	1.20	0.18	0.00304	-0.003		

Table 6. Isothermal studies of copper adsorption on the third composite film

C_0 mg/l	C_e mg/l	Q_e mg/l	Ce/q_e	$Ln\ Ce$	$Ln\ q_e$
10	2.00	8.00	0.25	0.69	-2.07
20	6.00	14.00	0.42	1.79	-2.63
30	12.00	18.00	0.66	2.48	-2.89
40	15.00	25.00	0.60	2.70	-3.21

C_0 represent initial concentration of copper ion

Ce represent metal equilibrium concentration of copper ion

Q_e represent equilibrium metal ion adsorbed concentration of copper ion

Table 7. Langmuir isotherm values of copper adsorption on third composite film

Langmuir isotherm	Values
C_e	6
K_L	0.16
q_e	44
Q_0	0.73

$C_e /q_e = 1/\ K_L\ Q_0 + C_e /\ Q_0$, Where C_e represent equilibrium metal concentration (mg/l), q_e represent equilibrium adsorbed amount of our study metal (mg/g), K_L represent Langmuir equilibrium constant (L.mg^{-1}), Q_0 represent maximum adsorption capacity (mg. g^{-1}).

Table 8. Freundlich isotherm values of copper adsorption on the third composite film

Freundlich isotherm	Values
Log q_e	1.64
Log C_e	0.77
n	1.07
Log K_f	0.947
K_f	9.47

Log (q_e) = Log (K_f) + 1/n Log (C_e), Where K_f represent freundlich constant (L.mg^{-1}), n represent heterogeneity

factor.

Table 9. Kinetic study of copper adsorption on the third composite film

Time min.	Q_t	Q_e	T/q_t	$Q_e - q_t$	$Log(Q_e-q_t)$
30	45	5	0.66	-40	-1.60
60	40	10	1.50	-30	-1.40
90	35	15	2.57	-55	-1.70
120	30	20	4.00	-10	-1.00
150	25	25	6.00	0	0.00
180	20	30	9.00	10	1.00
210	15	35	14.00	20	1.30
240	15	35	14.00	20	1.30
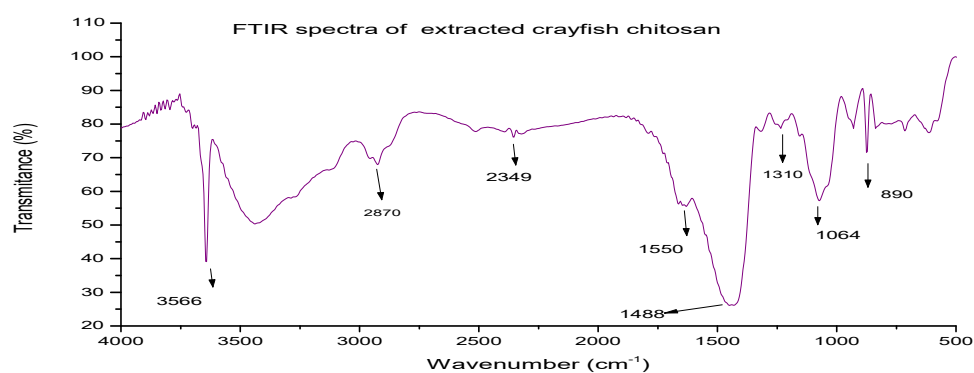
Fig. 1.   **FTIR spectra of extracted chitosan from _Procambarus clarkii_**
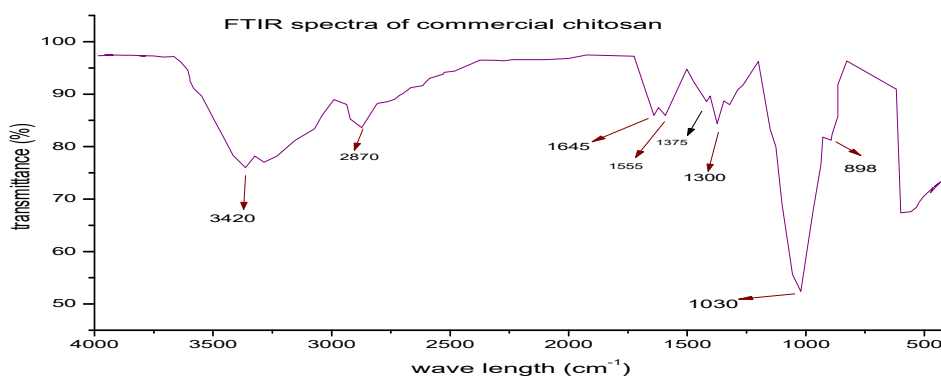
Fig. 2. FTIR spectra of a commercial chitosan
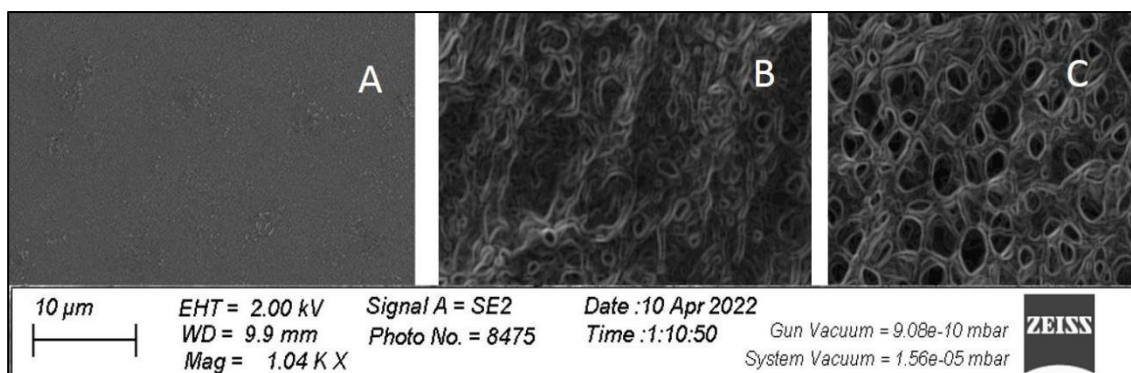
Fig. 3. SEM photos of the three composite films prepared from exoskeletons of *Procambarus clarkii*

A: resemble SEM photo of the first prepared film, B: resemble SEM photo of the second film, C: resemble SEM photo of the third prepared one.
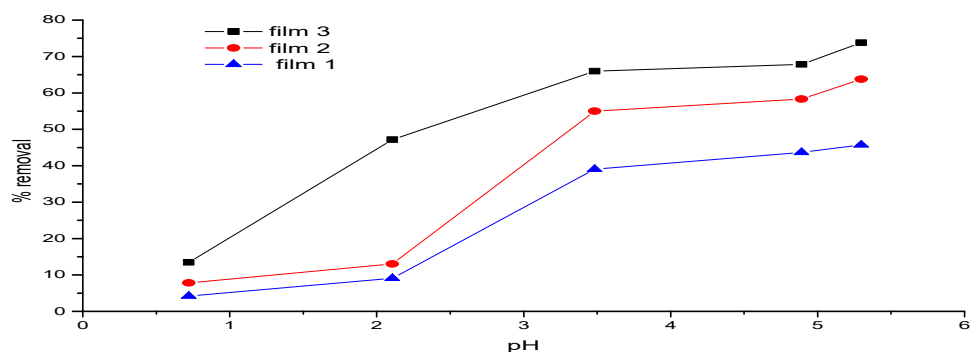
Fig. 4. Effect of pH parameter on adsorption capacity of the three prepared composite films
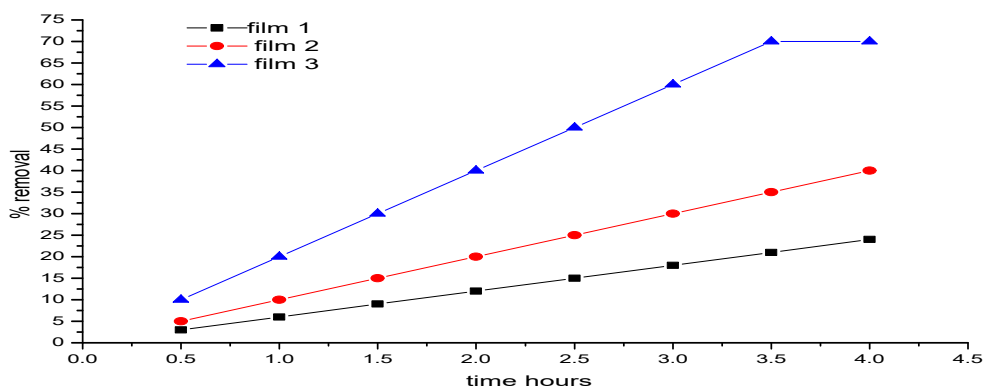
Fig. 5. Effect of time variation on adsorption capacity of the three prepared composite films
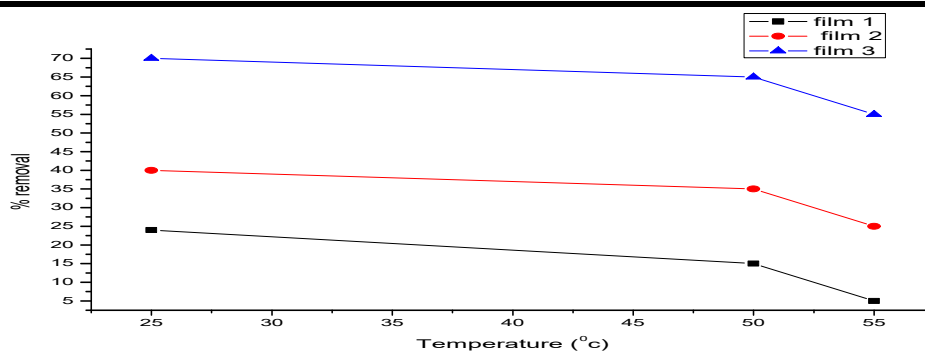
Fig. 6. Effect of temperature variation on adsorption capacity of the three prepared composite films
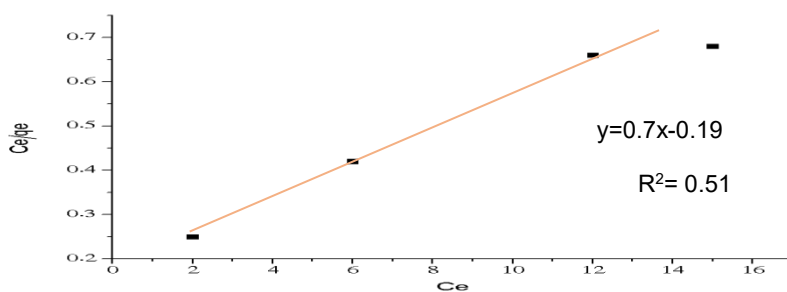
Fig. 7. Langmuir isotherm model for adsorption of copper on the third prepared film
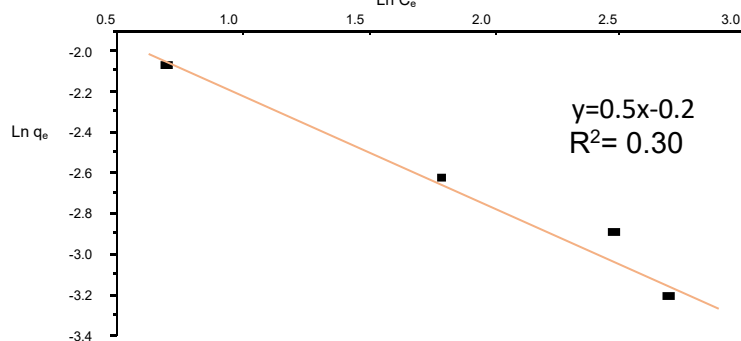
Fig. 8. Freundlich isotherm model for adsorption of copper on the third prepared film
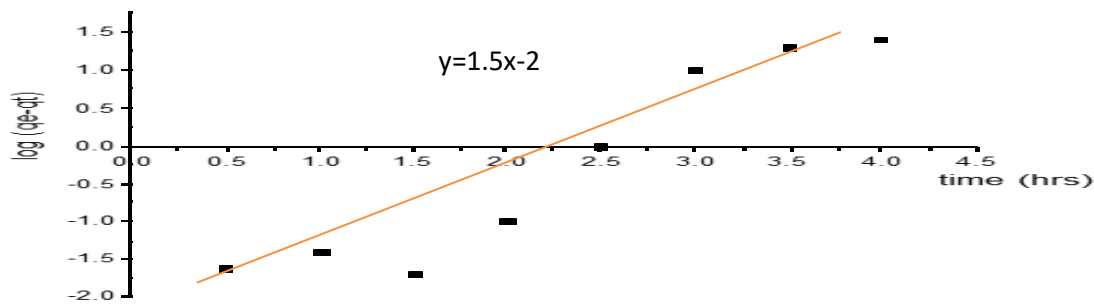
Fig. 9. Pseudo first order kinetic study for adsorption of copper on the third prepared film
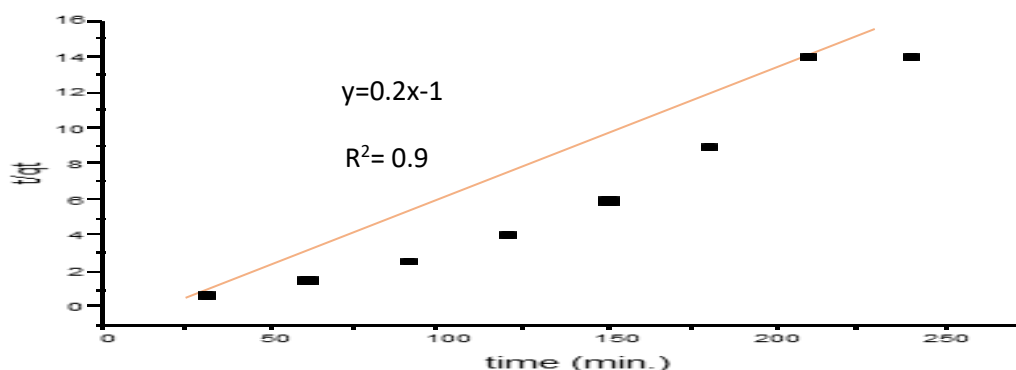
Fig. 10. Pseudo second order kinetic study for adsorption of copper on the third prepared film

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