Preparation and Characterization of Periwinkle Shell Based Chitosan-Kenaf fibre Copolymer and its Derivatives for Selective Binding of Cu (II) and Zn (II) ions from Electroplating Effluent

*[1]SAMUEL, AE; [1]KAMBA, SY; [1]SAMAILA, DS; [2]ILESANMI, NY

*[1]Department of Chemistry, Federal University of Agriculture, Zuru, Kebbi State-Nigeria
[2]Department of Chemical Sciences, Mountain Top University, Ibafo, Ogun State-Nigeria

*Corresponding Author Email: seaadeiza@yahoo.com
*Tel: +234-8032421643

Co-Authors Email: chemsky001@gmail.com; bondesamaila@gmail.com; nathanaelilesanmi40@gmail.com

ABSTRACT: The levels of heavy metal in industrial waste streams, if not remediated before discharge to eco-system, could pose a threat to flora and fauna. The objective of this study was to evaluate the suitability of a novel adsorbent materials from periwinkle shell-based chitosan-kenaf fibre copolymer and its ethylene glycol diglycidyl ether crosslinked derivatives for the selective removal of Cu^{2+} and Zn^{2+} from electroplating effluent using batch experimental protocol. Results showed that the crosslinked copolymers were more effective for the sorption of these metal ions from effluent solution with percentage sorption range of 76-87% and 84-93% for Cu^{2+} and Zn^{2+} respectively. Kinetic data depicts pseudo-second-order model fits for the adsorbent materials and confirm chemosorption as the mechanism for metal ion complexation with adsorbent surfaces. Based on R^2 correlation values, sorption of the metal ions by the pristine adsorbent materials fit well with Langmuir isotherm model, in contrast, those for crosslinked adsorbent materials were best described by Freundlich isotherm model. The results present the adsorbent materials with auspicious potentials, especially the crosslinked derivatives, and stand them in exceptional good stead as suitable bioresource materials for column packing in waste abatement equipment for remediation of these metal ions from electroplating effluent solution.

Globally, interest in environmental sustainability has elicited response in the use of biomass as low-cost sorbent materials for removal of pollutants from waste streams. In recent years, biopolymers have attracted immense research attention in their application as adsorbent materials for the remediation of heavy metals from industrial waste streams Samuel, *et al.,* (2019). Heavy metal contamination of water resources is of great concern owing to their deleterious effect on flora and fauna even at low concentration Kadirvelu *et al.*, (2000); Descalzo *et al.*, (2003). The main source of heavy metal contamination is from various industrial activities such as metal plating, mining operations and electric device manufacturing Lee *et al.,* (2001); Xiao and Thomas, (2005). Heavy metal such as nickel, arsenic, mercury, zinc, chromium and copper are documented in the U.S.A. Environmental Protection Agency list of pollutants (Cameron, 1992). The non-biodegradable nature of these metal ions necessitates their effective removal from aqueous media through various physical and chemical (chemical precipitation, solvent extraction, ion exchange and adsorption) technologies for the preservation of environmental quality and public

health (Onwuka, *et al.,* 2022). Sorption of heavy metal ions using biomass has emerged as an attractive method for the remediation of these metal ions from waste effluents, owing to their unique properties, ubiquitous, low cost, effective in trace metal level and easy to regenerate for use Babel and Kurniawan, (2003); Olayinka,*et al.,* (2007). Chitosan a derivative obtained from the deacetylation of chitin- a naturally abundant glucose-amine copolymer from crustaceans, has particularly attracted interest due to its ability to chemically coordinate or physically adsorb various heavy metal ions Castro Dantas *et al.,* (2001); Vincent and Guibal, (2001); Rhazi *et al.,* (2002). The crystalline nature of the glucose-amine copolymer limits its potency for adsorption of metal ions Li and Bai, (2006). Chitosan hydrogel beads have been produced to reduce crystallinity and improve sorption of heavy metal ions Yan and Bai, (2005).

The major drawback of the chitosan hydrogel beads is its poor resistance to low pH values and tensile properties. Attempts have been advanced to ameliorate the chemical stabilities and tensile properties of chitosan hydrogel beads by chemical crosslinking with epichlorohydrine, glutaricdialdehyde and ethylene glycol diglycidyl ether Wan Ngah *et al.,* (2002).

Electroplating is one of the industrial applications of electrolysis, used for the coating of metal surface for aesthetics and luster. However, this industrial process leaves behind effluent stream loaded with alkali and heavy metals ions amongst other things. It is imperative to produce an adsorbent material characterized with, high porosity, large surface area and effective strength endowed with good chemical and mechanical stabilities for remediation of these metal ions from the effluent stream before discharge to the environment. Therefore, this paper presents the use of a novel periwinkle shell chitosan-kenaf fibre copolymer and its ethylene glycol diglycidyl ether crosslinked derivatives for the selective sorption of Cu^{2+} and Zn^{2+} from electroplating effluent.

MATERIALS AND METHODS

Collection and pretreatment of periwinkle shell: Periwinkle shells were obtained from Lagos Island Market, Lagos-Nigeria. The shells were washed in a running tap water repeatedly, to remove sand and other foreign matter.

The washed shells were then air-dried for two weeks (14 days). The dried shells were then milled with a hammer mill (Model; HM560) for 6h and ball milled (Model: BM222) for 12h into fine powdered particle. The periwinkle shell powder was fractionated with a

25micron sieve and stored in polyethylene bags at ambient temperature.

Preparation of Periwinkle Shell based Chitosan: 50 g of periwinkle shell powder was weight out of the stock and placed in a 250ml conical flask and 100ml of 10% HCl was aggregated into the flask at room temperature, and left to stand for 24h. The flask and it content was then placed in a shaker at 100 rpm for 30 minutes after which the content of the flask was filtered (Whatman #42). The demineralized periwinkle powder was washed repeatedly, with distilled water until neutral to litmus. The off white demineralized powdery substance was deprotienized in 250ml beaker, by adding 10%NaOH and heating at 80°C for 12h with continuous stirring (100 rpm) on a thermostatic heating mantle. The deprotienized powder was washed with distilled water until neutral to litmus. The sample was then decolourized, by adding 50ml acetone and allows standing for 4h. The chitin was rinsed with ethanol, distilled water and dried in an oven set at 105°C for 2h. Deacetylation of the chitin was achieved by placing 10g of the chitin sample in 250ml conical flask with addition of 50%NaOH and agitated in a magnetic stirrer at 250 rpm for 5h, after which the flask was stopped with aluminum foil and allow standing for 72h. The mixture was washed with distilled water repeatedly until neutral to litmus, filtered (Whatman #42) and oven dried at 105°C. The periwinkle shell chitosan was off white flakes.

Collection and pretreatment of kenaf fibre: Kenaf fibre was obtained from harvested stems in a garden within the premises of the Federal University of Agriculture, Zuru. The stem bark was peeled off, washed with distilled water and dried at 50°C for 6h. The peel was steeped in 5% NaOH solution for 48h, rinsed with 1% acetic acid solution and washed with distilled water until neutral to litmus, and dried in an oven set at 105°C for 12h. Kenaf fibre was obtained by ball milling the treated peels and fractionated (25μm), before storage in a polyethylene bag.

Preparation of Periwinkle Chitosan-Kenaf Fibre Copolymer: 5g of periwinkle chitosan was weighed into 250ml beaker; 100ml of 2% acetic acid was added. The beaker and its content were placed on a magnetic stirrer (stirred at 200rpm) set at 70°C for 4h. 5g of kenaf powder was then added to the beaker and the mixture was stirred (250rpm) at 30°C for 3h. The reaction mixture was then poured into a 100ml 1.0MNaOH solution contained in a 500ml beaker to form the copolymer (50 wt.% chitosan- 50 wt.% kenaf fibre). The beaker and its content was stirred (50rpm) for 8h at ambient temperature to allow for

SAMUEL, A. E; KAMBA, S. Y; SAMAILA, D. S; ILESANMI, N. Y.

solidification of the copolymer mass. The copolymer was then removed and washed with distilled water until neutral to litmus. The same procedure was used for other preparations (2.5g of chitosan and 7.5g of kenaf for 25 wt. % chitosan- 75 wt. % kenaf fibre and 7.5g of chitosan and 2.5g of kenaf for 75 wt. % chitosan– 25 wt. % kenaf fibre).

Crosslinking of Periwinkle based Chitosan-Kenaf Fibre Copolymer: 5g of Periwinkle based Chitosan-Kenaf Fibre Copolymer was weighed into a 500ml conical flask containing 50ml of 20% formaldehyde solution. The flask and its content was placed on a magnetic stirrer set at 30^0C and operated at 250rpm for 2h. The ensuing solution was allowed to stand in a seperatory funnel for 24h; the formaldehyde treated copolymer was then recovered from the supernatant. The copolymer was then washed repeatedly with distilled water, until free of formaldehyde Li and Bai, (2005).

5g of formaldehyde treated copolymer was weighed into a 250ml beaker containing 50ml of distilled water. The pH adjusted to 10 using 0.1MNaOH and stirred (50rpm) on a magnetic stirrer for 20min., 1g of ethylene glycol diglycidyl ether (EGDE) was added and reaction was allowed to proceed at 80°C for 5h and stirred (50rpm). The reaction mixture was cooled to ambient temperature, and the crosslinked copolymer (50 wt.% chitosan- 50 wt.% kenaf fibre-c-EGDE) was washed with distilled water to pH 6.5. 5g of crosslinked copolymer was added to 500ml conical flask containing 100ml of 0.5 M HCl solution, the flask was placed on a magnetic stirrer set at 30^0C and operated at 250rpm for 6h. The HCl treated crosslinked copolymer was recovered with a seperatory funnel and washed with distilled water repeatedly until neutral to litmus. The same procedure was carried out to prepare other samples (25wt.% chitosan-75wt.% kenaf fibre-c-EGDE and 75wt.% chitosan-25wt.% kenaf fibre-c-EGDE).

Physico-mechanical properties of copolymer: The adsorbent materials were characterized for their percentage swelling, dissolution, hydration rate and tensile properties.

Determination of percentage swelling: The swelling ratios of the adsorbents were assessed in three different solvents; 1% NaOH 1% H_2SO_4 and 1% NaCl. The solvent uptake by the copolymer adsorbent materials was determined by the pat-and-weigh method Samuel *et al.,* (2019). Copolymer mass after measuring their dry weight were placed in the solvents contained in a standard test-tube and stopped with aluminum foil, Three samples were used for each

study. The swelling mass ratio (q_m) after equilibration for 24h was evaluated using the equation 1.

$$\text{Percentage swelling} = \frac{M_1}{M_2} \times 100 \quad 10$$

Where M_1 and M_2 represents mass of dry and swollen copolymers respectively.

Dissolution studies: The dissolution studies for the adsorbent copolymer materials were evaluated in the following solutions; 0.1M NaOH, 0.1M HCl, 0.1M KCl and Distilled water respectively. 0.2g of each sample was taken into a conical flask, and aggregated with 20ml of the solution; the flask was fitted into a shaker set at 100rpm for 24 h. At the end of agitation the flask and its content was allowed to stand for 1h, and the nature mixture was observed.

Hydration studies: Hydration studies of copolymer samples were determined according to ASTM D 570-98 (2010). Prior to water absorption measurements, the samples was dried over silica gel for 48 h. Water absorption was studied by soaking 2g (three samples were used for each study) of copolymer sample in distilled water. The samples were whole immersed each in 200ml distilled water in a 250ml beaker. At regular intervals, each sample was removed, dried with cotton wool, and weighed to determine its water absorption. The measurements were repeated until saturation of the samples was attained. The hydration rate (H_r) was calculated according to the equation 2:

$$\text{Hr (\%)} = \frac{W_2 - W_1}{W_1} \times 100 \quad (2)$$

Where W_1 and W_2 are the weights of dried and water saturated sample respectively.

Determination of tensile properties: Copolymer samples for study of tensile properties were of dimensions 50 mm x25 mm x 2mm and according to ASTM D 1621-10 (2010) and dried over silica gel for 48h before mechanical test. A universal testing machine (Saumya 3382), the machine capacity is 100 kN with 1:100 kN force ranges. A tensile strain rate of 0.1 per min and a deflection rate of 2 mm/min were used for the tensile properties. The readings for three samples were determined, and the mean and standard deviation recorded.

Collection of electroplating effluent: Electroplating rinse wastewater was obtained at the electroplating shop floor of the Federal Institute of Industrial Research, Oshodi-Lagos, Nigeria. 250ml each of effluents solution were obtained from four suction points that leads to the effluent reservoir tank. They

were homogenized to 1000ml effluent solution in a 2000ml Erlenmeyer flask to obtain a stock solution. Physico-chemical properties of the effluent solution namely; conductivity, dissolved solid, total solid, acidity, p^H, alkalinity, dissolved oxygen, chemical oxygen demand and suspended solid were determined by standard test methods as outlined by Friberg *et al.,* (1986). Effluent concentrations; 50ppm, 100ppm, 150ppm, 200ppm and 250ppm, were prepared from the stock by serial dilution.

Batch adsorption experiment: Sorption parameters remarkably; adsorbent dosage (1.0g, 1.5g, 2.0g, 2.5g, and 3.0g), equilibrium sorption time (30min, 60min, 90min,120min and 150min), effect of pH (2, 4, 6, 8, and 10) and effect of temperature (30ºC, 40 ºC, 50 ºC, 60ºC and 70ºC) was studied using standard procedure (20ml effluent stock solution and 100rpm stirring speed on a magnetic stirrer). In each case, the residual metal ion concentration absorbed was quantified with Perkin Elmer Model 3110 Atomic Absorption Spectrophotometer. The sorption percentage and sorbed metal ion at equilibrium were evaluated using equations 1 and 2 respectively.

$$S\,(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (3)$$

$$q_e = \frac{(C_o - C_e)v}{m} \quad (4)$$

Kinetic and isotherm studies: 2.5g of copolymer materials was added to 20ml 50ppm effluent solution contained in a 250ml volumetric flask stopped with aluminum foil and equilibrated in a magnetic stirrer at 100rpm for 90 min. The same protocol was repeated for other effluent concentrations, in each experimental run the content of the flask was filtered and the filtrate aspirated in a Perkin Elmer Model 3110 Atomic Absorption Spectrophotometer and analyzed for metal ions concentration. The values of q_e and C_e were obtained for each investigation and processed with MATLAB software (version 4.0). The pseudo first and pseudo-second order kinetic models were employed to study kinetics of these metal ions sorption from the effluent solution Onwuka *et al.,* (2022)

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303}\right)t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad 6$$

The expression used for Langmuir isotherm Meng-Wei *et al.,* (2013);

$$\frac{C_e}{Q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad 7$$

A plot of (C_e/Q_e) vs C_e gave a straight line and the values of q_{Max} and b were calculated from the slope and the intercept respectively. Freundlich equation used for this study Meng-Wei *et al.,* (2013) was

$$Inq_e = InK_F + n^{-1}InC_e \quad 8$$

A plot of lnq_e vs lnC_e gave a straight line wherefrom the values of n and k_F were obtained from the slope (n^{-1}) and the intercept (lnk_F) respectively.

RESULTS AND DISCUSSION
The physicochemical parameters of the electroplating effluent solution as obtained from the electroplating shop floor of the Federal Institute of Industrial Research, Oshodi-Lagos are presented in table 1.

Table 1: Physicochemical properties of electroplating effluent sample

Parameter	Value
Conductivity	191.30 µs
Dissolved oxygen	4.25 mgL^{-1}
Total solid	0.61 mgL^{-1}
Cu^{2+}	17.45 mgL^{-1}
Zn^{2+}	21.26 mgL^{-1}
Acidity	93.10 mgL^{-1}
p^H	3.52
Alkalinity	7.40 mg NaOH L^{-1}
Chemical oxygen demand	1431 mgO$_2$L^{-1}
Dissolve solid	0.44 mgL^{-1}
Suspended solid	0.26 mgL^{-1}

The result shows that the effluent solution is acidic judging, by the acidity and p^H values which could be attributed to acid pickling of tarnished metal surface before plating Friberg, (1986). The conductivity and dissolved solid values suggests the presences of cations and anions species in the effluent solution. The concentration of the adsorbate are higher than permissible limit (<1ppm) of discharge to the environment (Forster and Wittman, 1983). The frequent usage of the galvanizing/hot dip line in the electroplating shop floor and suction of the effluent may characterized the higher concentration of Zn^{2+}. The slight alkalinity of the solution could be attributed to degreasing of pickled metal with caustic soda in electroplating vats Golomb, (1972). The presence of passivation rinses, mostly chromium compounds in the electroplating effluents solution may be attributed to the recorded values for the total solid, suspended solid and chemical oxygen demand. The values for the physico-chemical parameters of electroplating effluent solution presented for this study are in range and consistent with those reported by Olayinka *et al.,* (2007).

SAMUEL, A. E; KAMBA, S. Y; SAMAILA, D. S; ILESANMI, N. Y.

Table 2: Hydration, Swelling and Tensile properties of Adsorbent materials

Adsorbent Material	Hydration rate (H_r)	% Swelling			Tensile Properties		
		1% H_2SO_4	1% NaCl	1% NaOH	T.S, (MPa)	T.M, (MPa)	E.B, (%)
25wt.%chitosan-75wt.%kenaf fibre	92.3±0.44	29.1±0.11	41.2±0.11	48.2±0.11	38.1±1.22	3.12±0.21	26.1±0.22
50wt.%chitosan-50wt.%kenaf fibre	95.1±0.51	25.6±0.21	37.3±0.31	42.4±0.33	41.5±0.09	2.81±0.33	22.4±0.24
75wt.%chitosan-25wt.%kenaf fibre	98.2±0.52	23.3±0.41	35.4±0.44	39.6±1.23	44.6±1.07	2.14±0.13	19.1±1.26
25wt.%chitosan-75wt.%kenaf fibre-c-EDGE	86.8±0.23	17.5±0.17	30.2±0.45	43.7±1.74	55.7±1.22	5.11±0.42	18.4±2.21
50wt.%chitosan-50wt.%kenaf fibre-c-EDGE	82.5±0.34	14.4±0.23	27.3±0.37	37.8±2.14	58.4±1.35	4.82±0.14	15.8±1.71
75wt.%chitosan-25wt.%kenaf fibre-c-EDGE	78.6±0.44	12.1±0.24	19.6±0.27	33.9±1.42	61.2±2.22	3.94±0.27	14.3±1.62

T.S, T.M and E.B represents Tensile Strength, Tensile Modulus and Elongation at break respectively

Table 3: Dissolution characteristics of Adsorbent Materials

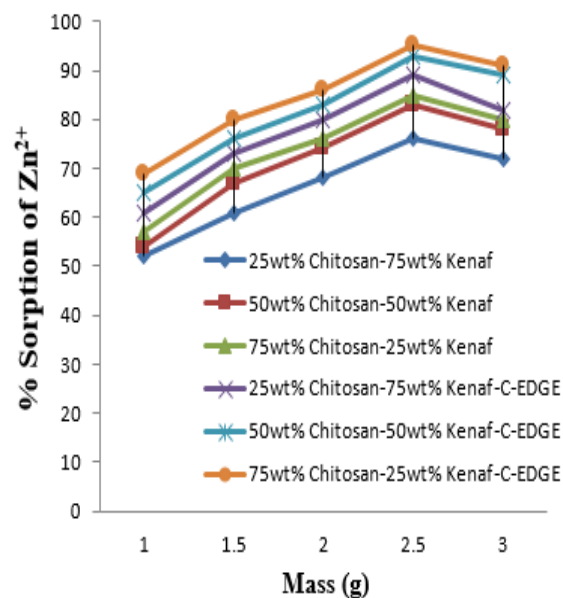| Adsorbent Material	Solvent			
	0.1M HCl	0.1M NaOH	0.1M CH_3COOH	Distilled water
25wt.%chitosan-75wt.%kenaf fibre	S	1S	S	IS
50wt.%chitosan-50wt.%kenaf fibre	S	IS	S	IS
75wt.%chitosan-25wt.%kenaf fibre	S	IS	S	IS
25wt.%chitosan-75wt.%kenaf fibre-c-EDGE	IS	IS	IS	IS
50wt.%chitosan-50wt.%kenaf fibre-c-EDGE	IS	IS	IS	IS
75wt.%chitosan-25wt.%kenaf fibre-c-EDGE	IS	IS	IS	IS

S = soluble; IS = insoluble

Tables 2 and 3 present some important properties for the characterization of adsorbent material. The hydration rates for the native copolymer increases as the percentage of chitosan and fibre content in the copolymer decreases and increases respectively. The decrease in chitosan and increase in fibre content concomitantly decreases the primary amine and increases hydroxyl groups on the adsorbent material. The increase in hydration rate may be ascribed to increase in hydrophilic OH groups.

The lower hydration values for the crosslinked adsorbent materials may not be unconnected with the occlusion of some hydroxyl moieties by ethylene glycol diglycidyl ether crosslinks Sudha, (2010) therefore, depleting this hydrophilic moiety on the adsorbent surfaces. The higher swelling of the pristine adsorbent copolymers in alkaline solution could be ascribed to partial mercerization of kenaf fibre making the cellulosic biopolymer more hygroscopic, and presumably alkaline hydrolysis of the predominant amine moieties in the glucose-amine copolymer in the absorbent samples Cheng *et al.,* (2009): Sudha, (2010).

The low swelling characterized by the crosslinked copolymer suggest the crystallization of the glucose-amine and cellulosic biopolymers into an infusible mass Samuel *et al.,* (2019). This low swelling behavior, high tensile properties, low elongation and

insoluble nature in acidic, alkaline and neutral solvents could be attributed to the combined effects of intra and inter-hydrogen bonds by amine and hydroxyl groups with ethylene glycol diglycidyl ether in the crosslinked copolymers. The effects of adsorbent dose on the removal of Cu^{2+} and Zn^{2+} from the effluent by the adsorbent materials are shown in figures 1 and 2 respectively.

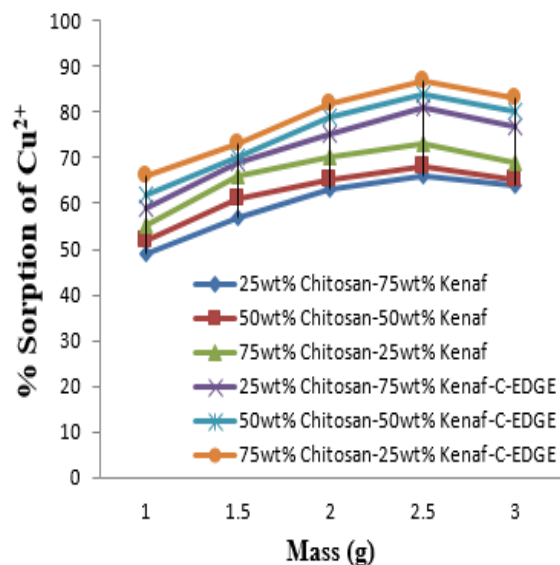**Fig 1**: Effect of adsorbent dosage on the sorption of Zn^{2+}

SAMUEL, A. E; KAMBA, S. Y; SAMAILA, D. S; ILESANMI, N. Y.

Fig 2: Effect of adsorbent dosage on the sorption of Cu^{2+}

For all the copolymer materials the sorption of the adsorbate increased rapidly with an increase in adsorbent load, characterized by a peak at 2.50g. The uptake of metal ions showed greater percentage sorption by the crosslinked materials albeit higher values for Zn^{2+} than Cu^{2+}. The higher values recorded for the crosslinked materials could be ascribed to the porosity of the crosslinked copolymer and the preponderance of primary amine and hydroxyl groups, shielded by formaldehyde and made available after treatment of the crosslinked copolymer with HCl Li and Bai, (2005).
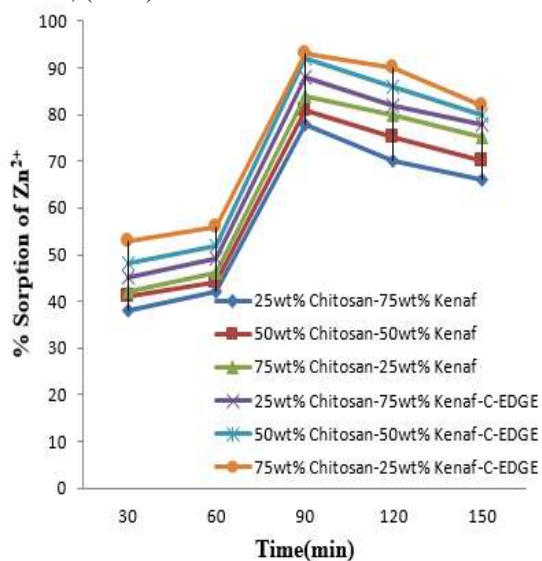

Fig 3: Effect of contact time on the sorption of Zn^{2+}

All these, confers mechanical stability, increased surface area and more sorption sites for ion-exchange reactions to the material. Beyond the threshold dosage,

and occasioned that electroplating effluent is a cocktail of metal ions amongst other things Samuel *et al.,* (2019), the coexistence of these adsorbate with alkali and alkaline earth metals ions in the effluent solution reduces the osmotic pressure between the adsorbate and adsorbent surface Osemeahon *et al.,* (2008). The decrease in osmotic pressure result to reduction in convection transport of these adsorbate metal ions to active sites. Thus, these alkali and alkaline earth metal ions in the effluent solution with higher reductive potential, diffuses and preferentially attached to available vacant sites thereby, constipates and out-played the complexation of the adsorbate with the adsorbent surface. Therefore, it is necessary for a pretreatment protocol targeted towards precipitation of these interfering ions for optimal performance of the adsorbent materials.
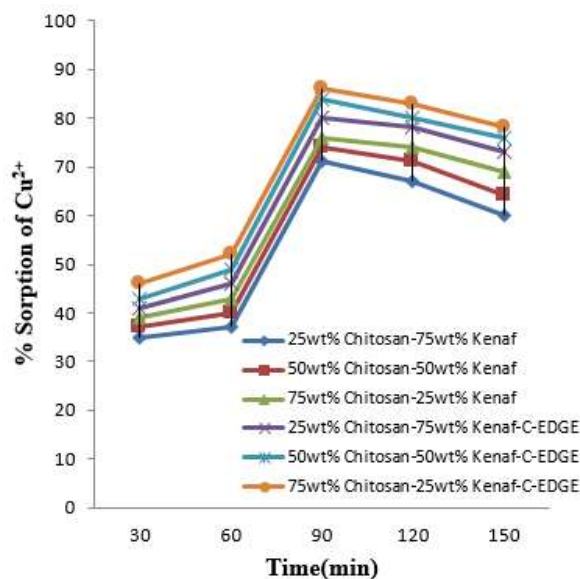

Fig 4: Effect of contact time on the sorption of Cu^{2+}

Equilibrium time is an imperative economic factor for design of effluent treatment flow process Olayinka *et al.,* (2007). The results as presented in figures 3 and 4 for the effect of contact time on the sorption of the adsorbate shows that over 70% of the metal ions rapidly accumulate and bind to adsorbent materials within 30minutes (60-90 minutes). Percentage sorption increases with a corresponding increase in contact time, before attainment of equilibrium at 90 minutes. This suggest an increase in contact time concomitantly increases diffusion of more adsorbate from the solution to vacant sites on the adsorbent surfaces and resulted in increased coordination of the adsorbate with the copolymer surfaces Li and Bai, (2005); Meng-Wei, *et al.,* (2013). The decrease in sorption efficiency after the equilibrium time could be adduced to decrosslinking of loosely held polymer

chains in the crosslinked copolymer Ramya, *et al.,* (2011); Samuel, *et al.,* (2019), and the fragmentation of uncrosslinked copolymer no thanks to prolong mechanical agitation, which resulted in the loss of metal ions to the bulk effluent solution.
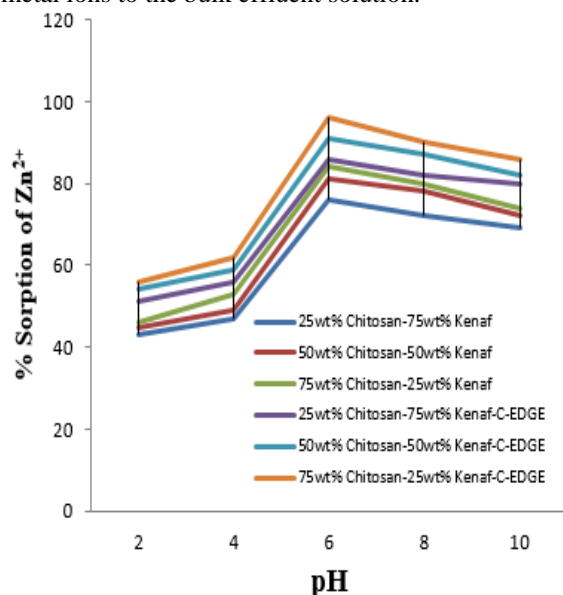

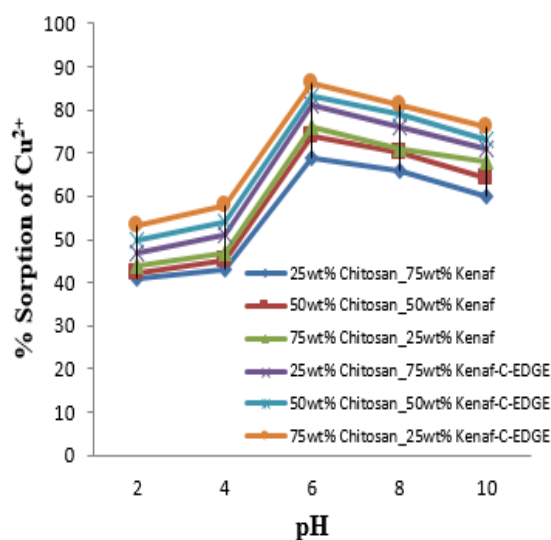**Fig 5:** Effect of pH on the sorption of Zn^{2+}

Fig 6: Effect of pH on the sorption of Cu^{2+}

Figures 5 and 6, shows the effect of p^H on the binding of the adsorbate on to the surfaces of the adsorbent materials. In general, the percentage sorption increases with an increased in p^H from the range 4 to 6 presenting 75wt.% chitosan-25wt.% kenaf-c-EDGE adsorbent material with maximum sorption efficiencies of 88% and 96% for Cu^{2+} and Zn^{2+} respectively. The highest sorption efficiencies recorded for the crosslinked derivatives could be attributed to the following: Shielding of primary amine

groups by formaldehyde prior to crosslinking reaction and their released by HCl after crosslinking Li and Bai, (2005). The preponderance of complexation moieties ($-NH_2$ and OH^-) on adsorbent surface and their relative stability to mechanical shear as evidence by their higher tensile properties substantiates their higher sorption efficiencies relative to the native adsorbent materials. The chemical equations below could best explain the chemistry for the sorption process Guibal, (2004); Dutta *et al.,* (2000).

$$-NH_2 + H^+ \leftrightarrow -NH_3^+ \qquad 9$$
$$-NH_2 + M^{2+} \leftrightarrow -NH_2M^{2+} \qquad 10$$
$$-NH_2 + OH^- \leftrightarrow -NH_2OH^- \qquad 11$$
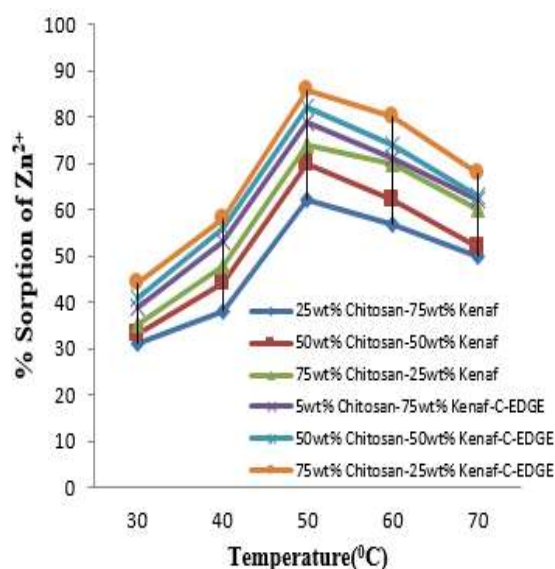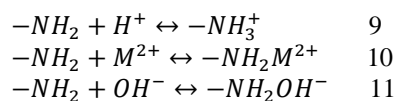
Fig 7: Effect of temperature on the sorption of Zn^{2+}

Fig 8: Effect of temperature on the sorption of Cu^{2+}

SAMUEL, A. E; KAMBA, S. Y; SAMAILA, D. S; ILESANMI, N. Y.
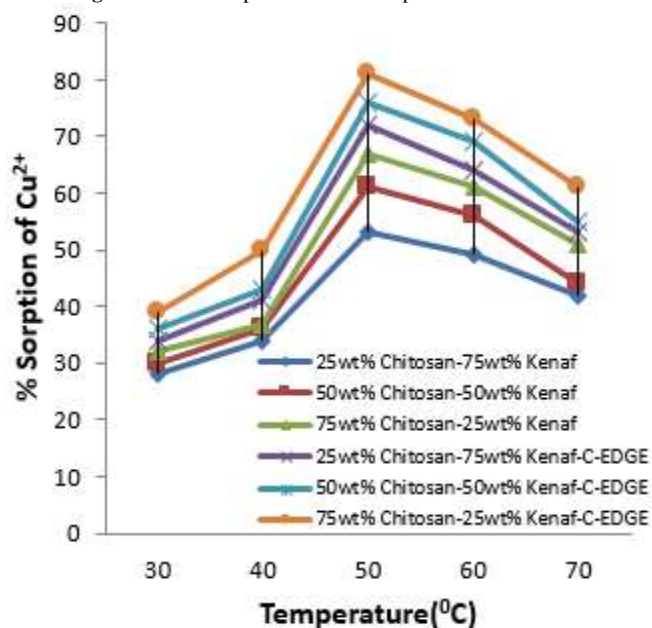
At low pH the forward reaction in equation 9, results to depleting of primary amine groups on the adsorbent surfaces owing, to protonation of the –NH$_2$ moieties Guzman *et al.,* (2002): Guibal, (2004) suggesting, that the low sorption percentages, may be ascribed to loss of adsorbent sites. As pH increases the backward reaction predominates and the concentrations of –NH$_2$ moiety on the adsorbent increases, and results in more electrostatic attraction and complexation of the adsorbate with copolymer surfaces as shown in equation 10. Increasing the solution pH above 6 resulted in electrostatic repulsion of these metal ions with adsorbent surface and precipitation of the adsorbate as metal hydroxide Prakash *et al.,* (2015), which suggests that at higher pH, equation 11 was the overriding chemistry controlling the sorption process.

The formation of metal hydroxide as precipitate was more pronounced for Cu^{2+} due to its insoluble character in excess alkaline media Prakash *et al.,* (2012), and affirms its lower sorption efficiency compare to Zn^{2+} within the range 8 to 10. At maximum p^H complexation and ion-exchange reaction mechanisms drives the binding of these metal ions from the effluent solution by these adsorbent materials. This finding is in concordance with competitive adsorption of Pb^{2+}, Cu^{2+}, and Zn^{2+} onto Xantate-Modified Magnetic Chitosan Zhu *et al.,* (2012). The effect of temperature on the efficiency of metal ion sorption by adsorbent surfaces is very important as thermal energy affects the mobility of metal ions in solution. From figures 7 and 8, sorption of metal ions increased with increase in temperature. Crosslinked adsorbent materials show higher sorption efficiency for both metal ions, which could be ascribed to increased thermal resistant owing to the presence of ethylene glycol diglycidyl ether crosslinks within the copolymers.

Temperatures above 50°C results in decreased metal ions uptake by the copolymer which may suggest the following: pulping of the cellulosic fibre at higher temperature Samuel *et al.,* (2019), facilitated by the slight alkalinity (7.40 mg NaOH L^{-1}) of the effluent, may results in diffusion of chelated metal ions from the swollen cellulosic polymer chains to the effluent solution and alkaline hydrolysis of primary amine groups at elevated temperatures Dutta *et al.,* (2004); Kumar *et al.,* (2013). These negative effects are expected to be less pronounced in the crosslinked derivatives. Therefore, substantiates the higher sorption efficiencies by the crosslinked adsorbent materials at elevated temperatures. The kinetic studies for sorption of metal ions by adsorbent surfaces shows the controlling mechanism guiding the removal of ions from aqueous solution. Table 4 presents the pseudo-first-order and pseudo-second-order kinetics experimental data. The R^2 values 0.3127-0.7743 and 0.3341-0.8892 for Cu^{2+} and Zn^{2+} respectively, reported for pseudo-first-order comparatively are less than 0.9789-0.9987 and 0.9771-0.9998 for Cu^{2+} and Zn^{2+} as presented for pseudo-second-order kinetic.

The corresponding rate constant for pseudo-second-order kinetic are much higher, by order of three magnitudes. Similarly, equilibrium quantity (q_e) for pseudo-second-order kinetic shows values for as much as two-fold as the corresponding values for pseudo-first-order kinetic. This suggests that metal ions from the effluent solution are more susceptible to coordination reaction with adsorbent surfaces over and above their physical attachment. The pseudo-second-order best fit implies that chemosorption was the controlling mechanism for the complexation of these metal ions with the adsorbent surfaces. These results are consistent with those reported by Prakash *et al.,* (2012); Onwuka *et al.,* (2022).

Table 4: Parameters for Pseudo first and second-kinetics order models

Adsorbent Material	Adsorbate	Pseudo-first order kinetics			Pseudo-second order kinetics		
		q_e (mgg^{-1})	$k_1 \times 10^4$	R^2	q_e (mgg^{-1})	$k_2 \times 10^1$	R^2
25wt.%chitosan-75wt.%kenaf fibre	Zn^{2+}	1.18	4.14	0.3341	3.45	5.16	0.9771
	Cu^{2+}	0.92	2.17	0.3127	1.76	4.08	0.9897
50wt.%chitosan-50wt.%kenaf fibre	Zn^{2+}	2.22	5.16	0.4246	5.66	6.11	0.9864
	Cu^{2+}	1.64	3.03	0.3349	3.32	5.21	0.9889
75wt.%chitosan-25wt.%kenaf fibre	Zn^{2+}	4.14	7.11	0.7271	11.14	8.24	0.9821
	Cu^{2+}	2.98	4.23	0.6984	8.84	5.76	0.9789
25wt.%chitosan-75wt.%kenaf fibre-c-EGDE	Zn^{2+}	6.13	8.19	0.8821	12.82	9.58	0.9992
	Cu^{2+}	4.09	5.42	0.7328	9.02	6.09	0.9987
50wt.%chitosan-50wt.%kenaf fibre-c-EDGE	Zn^{2+}	7.55	10.44	0.8643	15.19	10.41	0.9894
	Cu^{2+}	5.27	7.98	0.7176	12.11	7.45	0.9879
75wt.%chitosan-25wt.%kenaf fibre-c-EDGE	Zn^{2+}	8.19	12.17	0.8892	17.22	12.16	0.9998
	Cu^{2+}	6.05	8.45	0.7743	13.47	8.03	0.9799

Table 5: Isotherm Parameters for metal ion sorption by copolymer adsorbent materials

Adsorbent Material	Adsorbate	Langmuir			Freundlich		
		q_{max}	K_L	R^2	K_F	N	R^2
25wt.%chitosan-	Zn^{2+}	26.33	0.334	0.9811	0.276	1.61	0.8772
75wt.%kenaf fibre	Cu^{2+}	15.76	0.235	0.9644	0.178	1.24	0.8342
50wt.%chitosan-	Zn^{2+}	28.92	0.365	0.9809	0.572	2.11	0.8799
50wt.%kenaf fibre	Cu^{2+}	17.43	0.273	0.9687	0.194	1.91	0.8544
75wt.%chitosan-	Zn^{2+}	31.02	0.379	0.9844	0.599	2.56	0.8824
25wt.%kenaf fibre	Cu^{2+}	20.22	0.327	0.9785	0.254	2.07	0.8663
25wt.%chitosan-	Zn^{2+}	36.05	0.581	0.8267	0.723	3.22	0.9889
75wt.%kenaf fibre-c-EGDE	Cu^{2+}	24.82	0.392	0.8199	0.366	3.05	0.9874
50wt.%chitosan-	Zn^{2+}	41.88	0.593	0.8357	0.798	3.62	0.9891
50wt.%kenaf fibre-c-EDGE	Cu^{2+}	26.83	0.453	0.8309	0.423	3.53	0.9884
75wt.%chitosan-	Zn^{2+}	44.40	0.644	0.8125	1.825	3.97	0.9997
25wt.%kenaf fibre-c-EDGE	Cu^{2+}	29.42	0.467	0.8136	0.499	3.79	0.9986

Isotherm models are use to validate the practical application of adsorbent materials, table 5 shows the isotherm parameters for Langmuir and Freundlich isotherm models. The pristine copolymers fits the Langmuir model judging by the R^2 values with 97% and 98% correlations for sorption of Cu^{2+} and Zn^{2+} respectively. This suggests the adsorption sites shows equal energies, affinities and enthalpy for the removal of these metal ions from solution and depicts monolayer coverage by the adsorbate Li and Bai (2006); Zhu *et al.,* (2012). The higher q_{max} values as recorded for Zn^{2+} is consistent with its high electropositivity and stronger affinity by adsorbent surface moieties. Metal ion sorption by the crosslinked derivatives fit the Freundlich isotherm model as evidenced by the R^2 values close to 99% correlation for both metal ions. This shows that sorption of the adsorbate onto the crosslinked copolymers presents with a multi-layer adsorption pattern occasioned by intra and inter-molecular crosslinks within the copolymers Li *et. al.,* (2002); Li and Bai (2005), thus corroborating the porous and heterogeneous nature of these surfaces. The highest K_F and n values recorded for Zn^{2+} indicates a greater driving force and complexation by this adsorbate with the heterogeneous surfaces of the crosslinked copolymer. This result is consistent with report for enhanced metal adsorption by a novel amine shielded surface crosslinked chitosan beads Li and Bai, (2005) and chemically crosslinked metal-complexed chitosan for comparative adsorptions of Cu^{2+}, Zn^{2+} and Pb^{2+} in aqueous medium Chen, *et al.,* (2009).

Conclusion: A novel copolymer adsorbent materials from periwinkle shell-based chitosan-kenaf fibre and their ethylene glycol diglycidyl ether crosslinked derivatives have been produced, characterized and applied as adsorbent materials for the removal of Cu^{2+} and Zn^{2+} ions from electroplating effluent with maximum sorption conditions determined. The kinetic data fits the pseudo-second-order kinetic model and corroborates chemosorption as the controlling mechanism. Metal ions uptake by the uncrosslinked copolymers fit well with Langmuir isotherm model, but on the contrary, the crosslinked derivatives were best described by Freundlich isotherm model. The study presents these copolymers as suitable adsorbent materials for selective removal of these metal ions from electroplating effluent stream.

REFERENCES

ASTM D 1621-10 (2010). Standard Test Method for Compressive Properties of Rigid Cellular Plastics.

ASTM D 570-98 (2010). Standard Test Method for Water Absorption of Plastics

Babel, S; Kurniawan, TA (2003). Low-cost adsorbents for Heavy metals uptake from contaminated Water: A Review. *J. Hazardous Mater*. 97: 219-243.

Cameron, RE (1992). Guide to Site and Soil Description for Hazardous Waste Site Characterization: Report EPA/600/4-91/029: US Environmental Protection Agency, US. Government Printing Office: Washington DC. Volume 1 Metals. Pp 121.

Castro-Dantas, TN; Dantas-Neto, AA; Moura, MCP; Barros-Neto, EL; Paiva-Telemaco, E (2001). Chromium Adsorption by Chitosan Impregnated with Microemulsion. *Langmiur*. 17: 4256-4260.

SAMUEL, A. E; KAMBA, S. Y; SAMAILA, D. S; ILESANMI, N. Y.

Chen, A; Yang, C; Chen, C; Chen, CW (2009). The Chemically Crosslinked Metal-Complexed Chitosan for Comparative Adsorptions of Cu^{2+}, Zn^{2+} and Pb^{2+} in Aqueous Medium. *J. Hazard. Mater.* 163; 1068-1075.

Descalzo, AB; Martinez-Manez, R; Radeglia, R; Rurack, K; Soto, J (2003). Coupling Selectivity with Sensitivity in an Intergrated Chemosensor Framework: Design of a Hg^{2+} Responsive Probe, Operating above 500nm. *J. Am. Chem. Soc.* 125: 3418-3429.

Dutta, PK; Dutta, J; Tripathi, VS (2004). Chitin and Chitosan Chemistry, Properties and Applications. *J. Scientific Indus. Res.* 63: 20-31

Forster, U; Wittman, GT (1983). Metal Pollution in the Aquatic Environment. 2nd Edition, Spiringer Verlag, New York. Pp 136.

Friberg, L; Nordberg, B; Vouk, VB (1986). Handbook on the Toxicology of Metals Volume II. Specific Metals. *Amsterdam Elsevier* Pp 234.

Golomb, A (1972). Application of Reverse Osmosis to Electroplating Waste Treatment. *Plating.* 59: 316-319.

Guibal, E. (2004). Interactions of Metal ions with Chitosan-based Sorbents: A Review. *Sep. Purific. Technol.* 38; 43-74.

Guzman, J; Sancedo, I; Navano, R; Revilla, J; Guibal, E (2002). Vanadium Interactions with Chitosan. Influence of Polymer Protonation and Metal Speciation. *Langmuir* 18: 1567-1573.

Kadirvelu, K; Fuar-Brasquet, C; Cloirec, PL (2000). Removal of Cu (II) and Pb (II) by Adsorption onto Activated Carbon Cloths. *Langmuir.* 16: 8404-8409.

Kumar, GY; Atul, G; Yadar, SA (2013). Chitosan and its Applications: A Review of Literature. *Inter. J. Res. Pharm. Biomed. Sci.* 4: 312-331

Lee, ST; Mi, FL; Shen, YJ; Shyu, SS (2001). Equilibrium and Kinetic Studies of Copper (II) ion uptake by Chitosan-Tripolyphosphate Chelating Resin. *Polymer.* 42: 1879-1892.

Li, N; Bai, RB (2005). A Novel Amine Shielded Surface Crosslinking of Chitosan Hydrogel Beads for Enhanced metal Adsorption Performance. *Ind. Eng. Chem. Res*. 44: 6692-6700.

Li, N; Bai, RB (2006). Development of Chitosan based Granular Adsorbents for Enhanced and Selective Adsorption Performance in Heavy metal Removal. *Wat. Sci. Technol*. 54: 103-113.

Li, W; Zhao, H; Teasdale, PR; John, R (2002). Preparation and Characterization of a Poly(acrylamidoglycolic acid-co-acrylamide) Hydrogel for Selective Binding of Cu^{2+} and Application to Diffusive Gradients in Thin Films Measurement. *Polymers.* 43: 4803-4809.

Meng-Wei, W; Chan-Ching, W; Chien-Min, C (2013). The Adsorption Study of Copper Removal by Chitosan-Coated Sludge Derived from Water Treatment Plant. *Polymers.* 4: 545-551

Olayinka, KO; Alo, BI; Adu, T (2007). Sorption of Heavy Metals from Electroplating Effluents by Low-cost Adsorbents II: Use of Waste Tea, Coconut Shell and Coconut Husk. *J. Appl. Sci.* 7 (16): 2307-2313

Onwuka, KE; Atase, OC; Okereke, SEO; Enenwa, NE; Ogbuchi, GI (2022). Removal of Heavy Metals (Pb^{2+}, Zn^{2+}, Cu^{2+}, Hg^{2+}, Co^{2+}, Cr^{3+} and Cd^{2+}) from Water by Trimethyl Phenyl Ammonium Cation (TMPA+) Based Organoclay: Experimental and Statistical Test. *J. Mater. Polym. Sci.* 2: 2-9

Osemeahon, SA; Barminas, JT; Aliyu, BA; Nkafamiya, II (2008). Application of grafted membranes for sorption of Cd^{2+}, Fe^{2+} and Zn^{2+} ions in aqueous solution. *Afri. J. Pure Appl. Chem.* 2 (3): 32-36.

Prakash, N; Srinivasan, L; Sudha, PN; Gopaland Rengnathan, N (2015). Influence of Clay on the Adsorption of Heavy Metals like Copper and Cadmium on Chitosan. *Environ. Sci. Pollu. Res.* 24: 47-55

Prakash, N; Sudha, PN; Rengnathan, NG (2012). Cu^{2+} and Cd^{2+} Removal from Synthetic Industrial Waste Water using Chitosan and Nylon 6. *Environ. Sci. Pollu. Res.* 19: 2930-2941

Ramya, R; Shanmugapriyal, A; Ramasibramanian, S; Sudha, PN (2011). Studies on Removal of Cr(VI) and Cu(II) ions using Crosslinked Chitosan-graft-Polyacrylonitrile Copolymer. *Inter. J. Environ. Sci.* 1: 1323-1338.

Rhazi, M; Desbrieres, J; Tolaimate, A; Rinaudo, M; Vottero, P; Alagui, A; Meray, AE (2002). Influence on the Nature of the Metal ions on the

Complexation with Chitosan. Application to the Treatment of Ligand Waste. *Europ. Polym. J.* 38: 1523-1530.

Samuel, AE; Nwankwo, IC; Ezebor, F; Ojuolape, AA (2019). Adsorption of chromium by brewer's spent grain-g-poly (acrylic acid-co-acrylamide) from electroplating effluent. *Afri. J. Pure Appl. Chem.*4: 45-56

Sudha, PN (2010). Chitin, Chitosan and Derivative for Waste Water Treatment. In S.K (Ed), Chitin, Chitosan and Oligosacharides and their Derivatives. CRC Press, London. Pp. 585.

Vincent, T; Guibal, E (2001). Cr (VI) Extraction using Aliquot 336 in a Hollow Fibre Module made of Chitosan. *Ind. Eng. Chem. Res.* 40: 1406-1411.

Wan Ngah, WS; Endud, CS; Mayanar, R (2002). Removal of Copper (II) ions from aqueous solution onto Chitosan and Crosslinked Chitosan Beads. *React. Funct. Polym.* 50: 181-190.

Xiao, B. Thomas, KM (2005). Adsorption of Aqueous metal ions on Oxygen and Nitrogen Functionalized Nanoporous Activated Carbons. *Langmuir.* 21: 3892-3902.

Yan, WL; Bai, RB (2005). Adsorption of Lead and Humic Acid on chitosan Hydrogel Beads. *Wat. Res.* 39: 688-698.

Zhang, X; Bai, RB (2003). Mechanism and Kinetics of Humic Acid Adsorption onto chitosan-coated Granules. *J. Colloid Interface. Sci.* 264: 30-38.

Zhu, Y; Hu, J; Wang, J (2012). Competitive adsorption of Pb (II), Cu (II) Zn (II) onto Xantate-Modified Magnetic Chitosan. *J. Hazardous Mater.* 22:155-161.