International Journal of Pharmacy and Biological Sciences
ISSN: 2321-3272 (Print), ISSN: 2230-7605 (Online)
IJPBS | Volume 8 | Special Issue 4- Chem Fest | 2018 | 49-56
2nd National Conference on Emerging Trends and Future Challenges
In Chemical Sciences-Chem Fest-18
Held at Shanmuga Industries Arts and Science College, Tiruvannamalai, 05th Oct 2018
| Seminar Proceedings | Research Article | Biological Sciences |Open Access |MCI Approved|
|UGC Approved Journal|

PREPARATION OF CHITOSAN OLIGOSACCHARIDE BASED BLENDS FOR THE EFFICIENT EXTRACTION OF HEAVY METAL COPPER FROM WASTEWATER

M. Gopalakrishnan[1], P. Venkatesh[1]*, T. Gomathi[2] and P.N. Sudha[2]
[1]PG and Research Department of Chemistry, Pachaiyappa's College, Chennai, Tamil Nadu, India
[2]PG and Research Department of Chemistry, D.K.M. College for Women, Vellore, Tamil Nadu, India

*Corresponding Author Email: gopi10680@gmail.com

ABSTRACT

The present work was aimed to investigate the efficiency of novel chitosan oligosaccharide/Polypropylene glycol (PPG)/Montmorillonite (MMT) Clay blend for removing the toxic heavy metal Copper (II) ion from aqueous solution by batch adsorption studies. Initially the chitosan oligosaccharide was mixed with Polypropylene glycol and MMT clay by sol gel method. The sample was prepared in the presence of crosslinker glutaraldehyde. The prepared sample was analyzed through FTIR and XRD studies. The FTIR results indicate that the chitosan oligosaccharide was mixed homogeneously with MMT and PPG through intermolecular hydrogen bonding. The XRD results elucidate the changes in the crystalline behavior of the prepared COS/PPG/MMT-GLU blend. Both FTIR and XRD results revealed a strong interaction among the three components. To evaluate the adsorption potential of the synthesized blend, the parameters such as pH, adsorbent dosage, contact time and initial Cu (II)ion concentration was investigated. The adsorption isotherms and kinetics of adsorption were elucidated. This work provides a practical and high-efficient method for water treatment at moderate concentration of toxic heavy metals.

KEY WORDS

Chitosan oligosaccharide, PPG, MMT clay, Glutaraldehyde.

INTRODUCTION

Water is a source of drinking and for domestic purposes for humans [1]. Water pollution caused by both organic and inorganic compounds is considered a serious environmental problem. Among these pollutants are alter the chemical properties of water and are lethal to aquatic flora, animals and human beings [2]. Heavy metals are the dangerous pollutants, which become extremely toxic in high concentrations are however needed in trace amounts. Some of the heavy metals are mercury, cadmium, arsenic, copper and chromium [3], which are the most toxic metals that have polluted our entire atmosphere [4].

Copper is used in industrial activities, such as copper mining and smelting, brass manufacture, petroleum refineries and electroplating. Above industries wastewater contains copper were discharged into the environment causes many diseases such as liver and kidney damage stomach oilments and intestinal distress [5,6], and also affect marine system like damage the gills, liver, kidneys, the nervous system and changing sexual life of fishes [7].

Therefore, the scientists and environmental engineers are facing a rough task of cost-effective treatment for the removal of heavy metals [8]. There are several discourses on the removal of heavy metals from wastewater such as precipitation, ultrafiltration, adsorption, ion exchange, reverse osmosis, oxidation, coagulation, flocculation and membrane filtration processes [9].

Among these, adsorption is potentially an attractive technology for heavy metal removal from wastewater and is simple, efficient, selective, cheap, environmentally friendly and reversible to some extent. Chitin, chitosan, chitosan oligosaccharide are the important biopolymers that come from crustacean shells and have the capability to attach variety of heavy metals [10]. In recent years, these biopolymers have gained important credibility because of their good performance, low cost and natural affinity [11]. In the present study, chitosan oligosaccharide (COS) was chosen for the removal of copper ions with suitable modifications.

COS has high functional bioactive material with a wide range of immune enhancement, antitumor effect, antibacterial function, and calcium absorption acceleration effect. Water solubility is one of the drawbacks of COS, which cannot be used for wastewater treatment. For that reason, chitosan oligosaccharide was modified by blending [12] with Polypropylene glycol (PPG) and montmorillonite (MMT) clay.

The prepared ternary blend of COS/PPG/MMT-GLU was characterized by FTIR and XRD studies. To find the removal efficiency of the prepared ternary blend in waste water treatment using batch method. The influence of contact time, pH, adsorbent dose and metal ion concentration on the removal of copper ions by COS/PPG/MMT blend was investigated, in addition to the evaluation of the isotherm and kinetics.

MATERIALS AND METHODS

Materials

The chitosan oligosaccharide was purchased from India Sea foods, Cochin, Kerala. chemicals namely the MMT clay, polyvinyl alcohol and glutaraldehyde were purchased from Sigma Aldrich, India and Thomas Baker Chemicals Private Ltd, Mumbai respectively. All the reagents used in the present research work were of analytical grade.

Preparation of chitosan oligosaccharide /polypropylene glycol/ monmorillonite clay blend

About 1g of the chitosan oligosaccharide (COS) was dissolved in minimum amount of water. A required amount of polypropylene glycol dissolved in minimum amount of water and MMT clay dispersed in water was added to the above prepared COS solution which was then kept under constant magnetic stirring. To this above solution, glutaraldehyde (5 mL) was added and continued stirring for about half an hour to get ternary COS/PPG/MMT-GLU blend and then finally poured into petri plates and dried.

CHARACTERISATION

Fourier Transform Infra-Red Spectral Analysis

Measurements were performed with Thermo Nicolet AVATAR 330 spectrophotometer in 4000 – 400 cm^{-1} wave length range using KBr pellet method.

X – Ray Diffraction Studies

X–ray diffraction (XRD) studies were performed using X-ray powder diffractometer (XRD – SHIMADZU XD – D1) using a Ni – filtered Cu Kα X–ray radiation source in the diffraction angle range of 0°C to 90°C.

Batch Adsorption studies

The optimum conditions for metal ion adsorption were determined by varying the parameters such as pH, adsorbent dosage and contact time. These parameters have immense effect on the adsorption efficiency of the adsorbent.

RESULTS AND DISCUSSION

FT-IR spectrum of pure Chitosan oligosaccharide (Figure 1). Broad absorption bands at 3419 cm^{-1} and 2927 cm^{-1} corresponds to O-H and N-H stretching vibrations and symmetric $–CH_2$ stretching vibrations respectively. The absorption bands present at 1641 cm^{-1}, 1560 cm^{-1}, 1384 cm^{-1} and 1145 cm^{-1} shows the presence of C=O stretching, NH_2 bending vibration, C-H deformation vibration and -C-O-C- in glyosidic linkage. The C-O stretching vibration band was appeared at 1078 cm^{-1}.

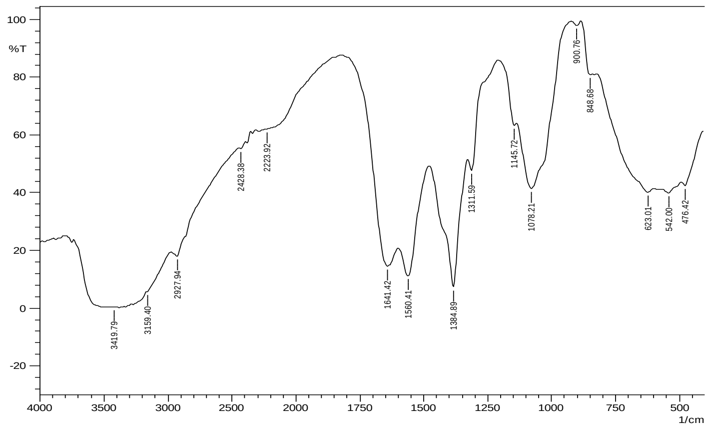

Figure 1: FT-IR spectrum of Pure COS

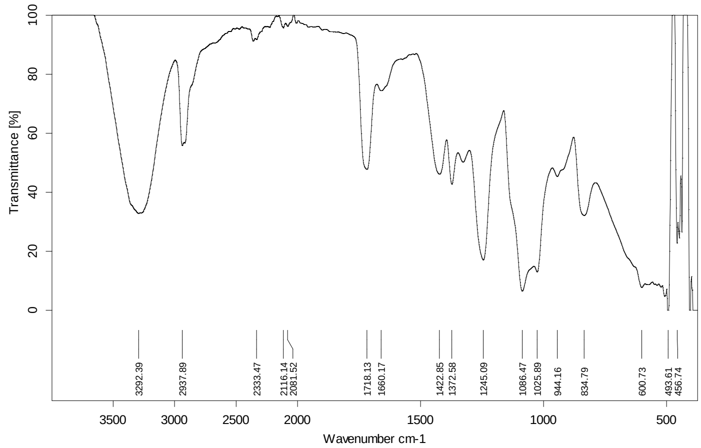

Figure 2: FT-IR spectrum of COS/PPG/MMT-GLU

The FTIR spectrum of COS/PPG/MMT-GLU blend of ratio (1:1:1) (Figure 2) showed a strong absorption band correspond to CH_2 bending, OH bending at 1372.58 cm^{-1}, 1422.85 cm^{-1} respectively will show the effectiveness of interaction between the chitosan oligosaccharide with the hydroxyl groups in polypropylene glycol. A band at 1163.52 cm^{-1} was assigned to the structure of saccharide. The blending of MMT clay was confirmed from the bands of Al-O and Si-O stretching vibrations at 1088.47 and 834.79 cm^{-1} respectively. As compared to pure COS, major characteristic bands and the change in intensity of band are important to confirmed by the interaction between COS, PPG and MMT was achieved successfully during blending.

XRD studies

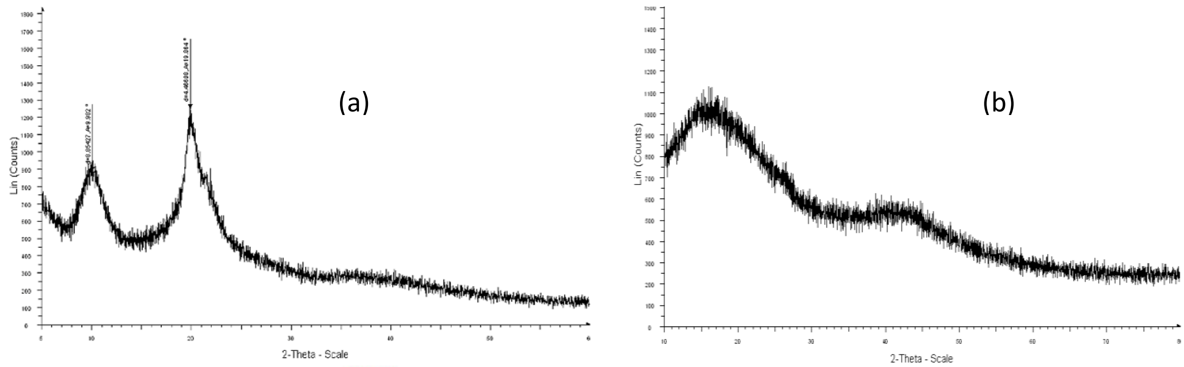

Figure 3: X-ray diffractogram of (a) pure COS and (b) COS/PPG/MMT-GLU blend

Figure 3a shows the X-ray diffractogram of pure chitosan oligosaccharide having two intense crystallite bands at 2θ values of 10 °, 20 ° with the percentage of crystallinity of 15.3 which indicates the semi-crystalline nature of chitosan oligosaccharide. **Figure 3b** shows the XRD diffractogram of COS/PEG/MMT-GLU blend. An intense peak was observed at 16° with a shoulder peak at 41.3°and the percentage degree of crystallinity was calculated to be 6.50 %. This shows that the prepared ternary blend has amorphous in nature due to disorderliness in their structure. Therefore, metal ion could easily penetrate through COS/PPG.MMT blend surface.

Batch adsorption studies

Effect of Contact Time

Experiments were conducted to test the effect of contact time on the adsorption process on to COS/PPG/MMT-GLU blend. The results indicated that the adsorption of Cu (II) increases on increasing the contact time. Rapid initial removal rate was observed because of the availability of sufficient vacant adsorbing sites. Afterwards, the percentage metal ion removal rate was decreased significantly due to the availability of limited vacant sites. The equilibrium adsorption was reached at 360 min. Further increase in contact time did not increase the uptake due to deposition of metal ion on the available adsorption sites on the adsorbent materials [13]. It is observed that remaining concentration of metal ions becomes asymptotic to the time axis after a definite interval of time and no further adsorption takes place in the batch experiments.

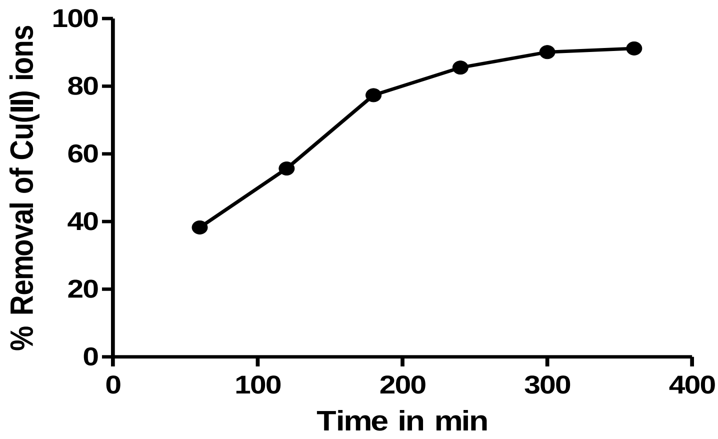

Figure 4: Effect of contact time

Effect of adsorbent dose

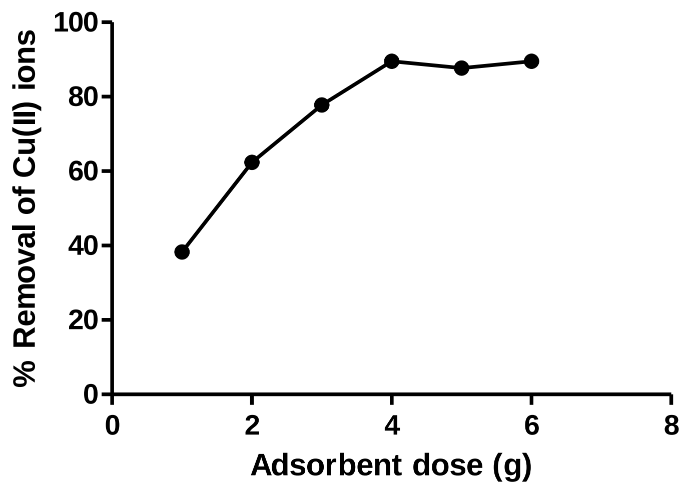

Figure 5: Effect of adsorbent dose

The effect of adsorbent dosage on the adsorption of copper (II) onto COS/PPG/MMT-GLU blend was investigated by varying the amount of prepared adsorbent from 1 to 6 g while keeping the other parameters pH (pH=6) agitation period (1 hr) and metal ion concentration (200 mg/L) as constant. From the figure 5, it evident that the percentage removal of Cu (II)ions increases with increasing the adsorbent dose. For Copper (II) ion, the percentage removal was increased from 38.3 % to 89.5 %. Further addition of the adsorbent beyond this did not cause any significant change in the adsorption. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles [14].

Effect of pH

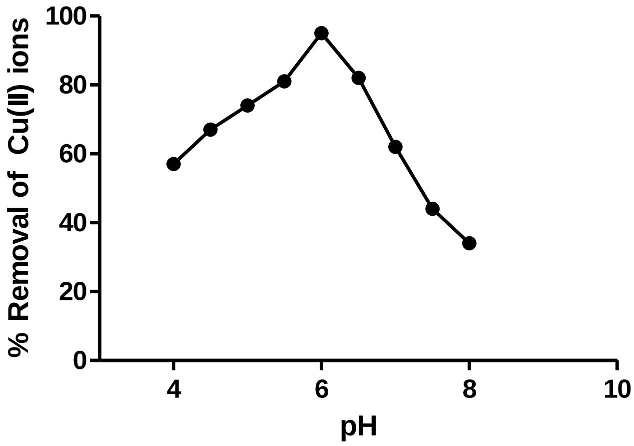

Figure 6: Effect of pH

Adsorption of metal ion was greatly influenced by the solution pH value, which concerns the solubility of metal ions, ion concentration of adsorbent functional groups and degree of ionization of the adsorbate in the reaction. The optimum pH for removal for Cu (II) ions was found to be 5. Therefore, in this study the pH was varied from 4 to 8 and the results are given in **Figure 6**. It was indicated that percentage removal of Cu (II) ions reached a maximum in a slight acidic medium and decreased in basic medium. The percentage removal of Cu (II) ions maximum 95% at pH 6. Also, in different pH ranges the surface charge on the adsorbent paved the way for effective removal of Cu (II) ions. Initially, while dissolving chitosan oligosaccharide, the primary amino group gets protonated (quaternized) and in acidic medium it is expected to have enhanced positive charge, This is due to the competition between protons and metal ions present in the aqueous solution. While increasing the pH, this competition will decrease, and the metal adsorption gets increases. Further increase in pH will lead to aggregation of chitosan oligosaccharide will lead to adsorption capacity decreases. The decrease in adsorption above optimum pH for COS/PPG/MMT-GLU is due to the precipitation of metal hydroxide complexes.

Adsorption isotherm

Langmuir isotherm

The Langmuir equation can be described by the linearized form as follows

$C_{eq}/C_{ads} = bC_{eq}/K_L + 1/K_L$

and $C_{max} = K_L/b$

Where

C_{ads} = amount of metal ions adsorbed (mg.g-^{1})

C_{eq} = equilibrium concentration of metal ion in solution (mg.dm^{-3})

K_L = Langmuir constant (dm^{3}.g)

b = Langmuir constant (dm^{3}.mg)

C_{max} = Maximum metal ion to adsorb onto 1g adsorbent (mg.g^{-1})

The calculated results of the Langmuir isotherm constants from figure 7 and C_{max} value are given in **Table-1**. The Langmuir isotherm model assumed that the absorbed layer was one molecule in thickness and that all adsorption sites had equal energies and enthalpies of adsorption.

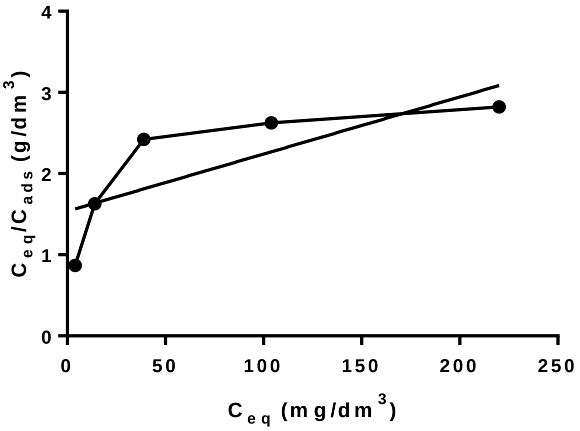

Figure 7: Langmuir adsorption isotherm plot for Copper (II)ion onto COS/PPG/MMT-GLU blend

Freundlich model

The widely used empirical Freundlich equation based on a heterogeneous surface is given by $\log q_e = \log K_F + 1/n \log C_e$

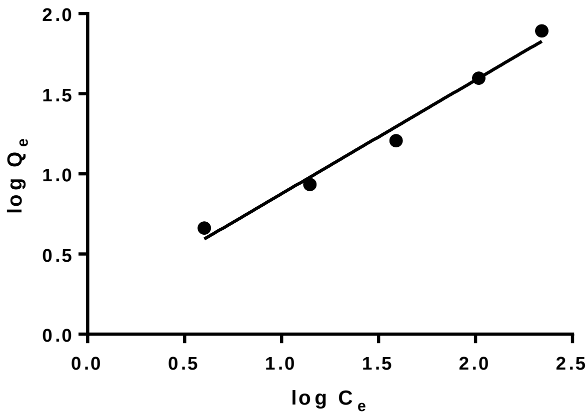

Figure 8: Freundlich adsorption isotherm plot for copper (II) ion on to COS/PPG/Clay glu(1:1:2) ternary blend

Where, KF and n are freundlich constants (mg/g). K_F and n can be determined from linear plot of log Ce against log qe (figure 8). The value of the correlation coefficient (R^2) for Copper ion was 0.9809, which is a higher value than that of Langmuir isotherm. Furthermore, the value of n lies between 1 and 10, it indicates a favorable adsorption.

Table 1: Adsorption isotherm constant

Metal ion	Langmuir Constants				Freundlich	Constants	
	K_L (dm³/g)	b (dm³/mg)	C_{max} (mg/g)	R^2	K_f (dm³/g)	n (dm³/mg)	R^2
Cu (II)	0.6506	0.00456	142.68	0.5994	1.4679	1.4098	0.9809

Kinetic Sorption Mechanisms

Pseudo-First-Order kinetics

The pseudo-first-order rate equation is given as

$\log (q_e-q_t) = \log q_e - K_1t/2.303$

Where, q_e and q_t are the amount of Cu (II) adsorbed on adsorbent (mg/g) at equilibrium and at time t, respectively, k_1 is the rate constant of first order adsorption min^{-1}. The straight-line plots of log ($q_e - q_t$) against t was used to determine the rate constant k_1 and correlation coefficient(R^2).

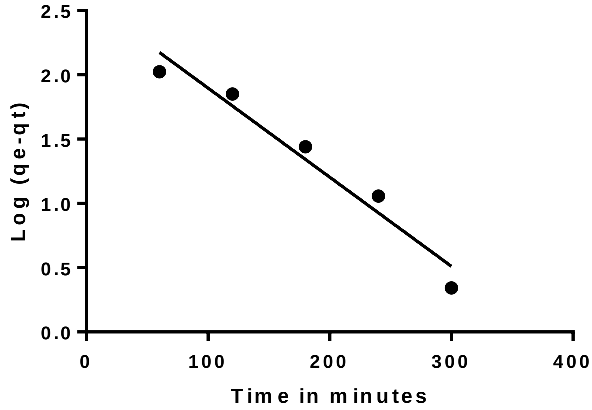

Figure 9: Pseudo-First-Order of Cu (II) sorption on to COS/PPG/MMT-GLU blend

Pseudo-second-order kinetics

The pseudo-second-order rate equation is given as

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

where q_e and q_t are the amounts of metal adsorbed (mg/g) at equilibrium and at time t

The linear plots of log (q_e - q_t) versus t and (t/q_t) versus t are drawn for the pseudo-first-order and the pseudo-second-order models, respectively. The rate constants k_1 and k_2 can be obtained from the plot of experimental data.

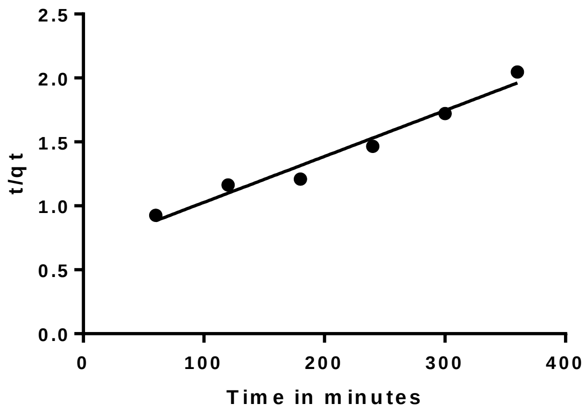

Figure 10: Pseudo-Second-Order of Cu (II) sorption on to COS/PPG/MMT-GLU blend

Table 2: Comparison of pseudo-first-order and pseudo-second-order kinetics constant

Metal ion	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	qe (mg/g)	**k_1 (min^{-1})**	**R^2**	**qe (mg/g)**	**k_2 ($g\ mg^{-1}\ min^{-1}$)**	**R^2**
Cu (II)	389.94	0.01596	0.9526	263.99	0.00002615	0.9813

The values of k_1 can be determined from the slope of the linear plot of log (q_e−q_t) versus t, and k_2 can be calculated from the slope of the linear plot t/qt versus t (Table 2, Figure 9 and 10). The pseudo-second-order linear plots resulted in higher R^2 values than the pseudo first- order. The values of q_e (cal) from the pseudo-second-order were closer to q_e (exp) than that from the pseudo-first-order. These indicated the better applicability of the pseudo-second- order model.

CONCLUSION

A potential COS/PPG/MMT GLU blend was evaluated for the sorption of Cu (II) from the aqueous solution. This study demonstrated that the variation of adsorbent dose, contact time, initial metal ion concentration and pH had a marked influence on the removal of Cu (II) ions from the aqueous solution. According to regression coefficient the Freundlich adsorption isotherm was better fitted than the Langmuir. The kinetics studies showed that the adsorption followed pseudo second order kinetics. Hence prepared ternary COS/PPG/MMT-GLU BLEND act as a good adsorbent and can be used for wastewater treatment.

REFERENCES

[1] Olaniran NS., Environment and Health: An Introduction, in Olaniran, N.S. et.al (Ed) Environment and Health. Lagos. Micmillan Nig. Pub. Co for NCF, 34-151, (1995).
[2] Fu F, Wang Q., Removal of heavy metal ions from wastewaters: a review. J Environ Manage. 92(3):407-18, (2011).
[3] Lazarova V, Bouwer H, Bahri A., Water quality considerations. In: Lazarova, V. and A. Bahri Editions. Water Reuse for Irrigation: Agriculture, Landscapes, and Turf Grasses. CRC Press, Boca Raton, Florida, USA, 31-60, (2005).
[4] Chehregani AB, Malayeri G, Golmohammadi R., Effect of heavy metals on the developmental stages of ovules and embryonic sac in Euphorbia cheirandenia. Pakistan Journal of Biological Sciences. 8:622-625, (2004).
[5] Carol Potera, Copper in Drinking Water: Using Symptoms of Exposure to Define Safety, Environ Health Perspect. 112(10): A568–A569, (2004).
[6] Pandey S, Chuwdhary AR, Tewari SR, et al., Trace elements in cervical mucus of infertile women. Indian Journal of Medicinal Research, 84, 163-166, (1986).
[7] Flemming CA, Trevors JT., Copper toxicity and chemistry in the environment: a review. Water, Air, & Soil Pollution, 44, 143–158, (1989).
[8] Ashutosh Tripathi and Manju Rawat Ranjan, Heavy Metal Removal from Wastewater Using Low Cost Adsorbents, J Bioremed Biodeg 6:6, (2015).
[9] Gunatilake S.K., Methods of Removing Heavy Metals from Industrial Wastewater, Journal of Multidisciplinary Engineering Science Studies (JMESS), Vol. 1 Issue 1, November - 2015
[10] Muzzarelli RAA., Chitin; Pergamom: Oxford, (1977).
[11] Krishna D, Padma Sree R., Artificial Neural Network and Response Surface Methodology Approach for Modeling and Optimization of Chromium (VI) Adsorption from Waste Water using Ragi Husk Powder, Journal Indian Chemical Engineer, 55 (3), (2013).
[12] Park JH, Saravanakumar G, Kim K, Kwon IC., Targeted delivery of low molecular drugs using chitosan and its derivatives. Adv Drug Deliv Rev 62: 28-41, (2010).
[13] Sivaksami MS, Gomathi T, Jayachandran V, Sudha PN., Preparation and characterization of nanochitosan for treatment wastewater. International journal of biological macromolecules, 57:204-212, (2013).
[14] Osu Charles I, Odoemelam SA., Studies on Adsorbent Dosage, Particle Sizes and Ph Constraintson Biosorption of Pb(II) and Cd(II) Ions from Aqueous Solution Using Modified and Unmodified Crassostrea Gasar (Bivalve)Biomass, International Archive of Applied Sciences and Technology, 1: 62-68, (2010)