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Removal of Lead (II) Ions from Aqueous Solution onto Chitosan Oligosaccharide-G-Glycidylmethacrylate / Polypropylene Glycol-Glutaraldehyde Blend

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Abstract

The main objectives of the present research is surface modification of chitosan oligosaccharide (COS) with glycidyl methacrylate (GMA) by grafting method using as ceric ammonium sulphate as a redox initiator in aqueous nitric acid medium. The synthesized graft copolymer (COS-g-GMA) was then blended with polypropylene glycol in 1:1 ratio in the presence of glutaraldehyde. Furthermore, the analyses of batch mode experiments were performed to study the experimental important parameters such as pH, metal ion concentrations, adsorbent dosages and contact time are also discussed. From the experimental data, the adsorption isotherms are well described by Langmuir and Freundlich model, the adsorption of heavy metals was fitted with Freundlich isotherm confirms the physical adsorption phenomena involved in this process. The kinetic parameter was correlated with the pseudo-second-order kinetic model. From the results, it was concluded that the novel hybrid material of COS-g-GMA/PPG-Glu blend is an excellent biosorbent for the removal of lead (II)ions from aqueous solution.

Keywords
Chitosan oligosaccharide, Glycidylmethacrylate, Glutaraldehyde, Ceric ammonium nitrate, Poly propylene glycol.

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INTRODUCTION

More recently, human actions are causing the slow implementation of plant and animal species through toxic pollution due to industrial and technological advancement. Heavy metal-containing water is one of the most toxic industrial wastes. Many studies have shown that heavy metals have been recognized as potential health and environmentally dangerous materials even at low concentrations [1].

Among these toxic heavy metals, Lead is pervasive in the environment and has hazardous effects on human health at high levels [2]. Lead adversely affects those that are most vulnerable in our society: infants, children, pregnant women, racialized individuals and individuals experiencing low income and poor nutrition [3,4] and their removal from industrial wastewater remain an important challenge. Hence, we had chosen lead metal ions for this study.

Adsorption−based technologies have proven to be more viable alternatives proposed for the treatment of industrial wastewaters containing heavy metals due to low cost of processing and instrumentation, simple operation and availability of different types of low−cost and environmental−friendly adsorbents **[5].**

The need for strong adsorbents has been emerged due to the escalation of industrial activity and environmental anxiety. To overcome this problem, numerous works have been done in order to extract effective materials by chemical treatment or chemical modification of fishery wastes. Hence, we had chosen chitosan oligosaccharide, which has been considered as most promising materials for heavy metal ion removal purpose as they exist abundantly and may form a cost-effective end product. It represents interesting and attractive adsorbent, because of their particular structure, physical and chemical characteristics, chemical stability and excellent selectivity towards metals. Modification of chitosan oligosaccharide with organic moieties results into improvement of its sorption abilities. An extensive research was done on modification of chitosan oligosaccharide by grafting and blending.

Chitosan oligosaccharide was blended with glycidyl methacrylate, which has the reactive double bond and epoxy group can form new functional groups by various chemical reactions and hence it was selected in this study for grafting process. The prepared copolymer was blended with polypropylene glycol in the presence of glutaraldehyde as cross-linking agent, which improves mechanical properties of the blend.

Based on the literature review an attempt has been made to utilize an inexpensive adsorbent system (chitosan oligosaccharide-graft-glycidyl methacrylate /polypropylene glycol- Glutaraldehyde) for the removal of toxic heavy metal lead(II) ions from aqueous solution using batch studies approach as a function of various parameters such as pH, adsorbent dose, contact time and initial metal ion concentration. The adsorption isotherms such as Langmuir and Freundlich models were used to fit with the adsorption equilibrium data and the adsorption kinetic models such as pseudo-first order, pseudo-second order were investigated.

MATERIALS AND METHODS

Materials

Chitosan oligosaccharide was obtained from India sea foods Cochin, Kerala, India. The monomer Glycidylmethacrylate was purchased from the Sisco research laboratory. Polypropylene glycol, Glutaraldehyde, sodium hydroxide and nitric acid were of analytical grade and used as received.

Methodology

The graft copolymerization of glycidyl mecharylate onto chitosan oligo saccharide with ceric ammonium nitrate as an initiator. The grafting parameters including the grafting efficiency, grafting percentage and % monomer conversion were systematically evaluated as function of temperature, monomer concentration, chitosan oligo saccharide concentration and reaction time.

From the results illustrated the effect of initiator, monomer and polymer concentration which showed the optimal concentration of Ceric ammonium nitrate, Glycidyl methacrylate and Chitosan oligosaccharide respectively were Ceric ammonium nitrate for 0.9 g, Glycidyl methacrylate for 0.8 mL and Chitosan oligosaccharide for 0.6 g. The optimum value sample was used further applications.

Preparation of Chitosan oligosaccharide – g- Glycidyl methacrylate (COS – g – GMA)

Chitosan oligosaccharide (0.6 g) was dissolved in 30 mL of water and the monomer glycidyl methacrylate (0.8 mL) was dissolved in minimum amount of ethanol. The above prepared solutions were mixed well and stirred continuously in magnetic stirrer to attain 80 °C. In order to initiate the polymerization process in the above mixture, about 10 mL of ceric ammonium nitrate (0.9 g CAN dissolved in10 mL of Nitric acid) was added. This mixture was stirred constantly at 80 °C for a period of 30 minutes. The resultant solution was cooled to room temperature and then it was poured into 2N NaOH to precipitate the product. The obtained graft copolymer was then filtered, washed with water for several times and then dried at room temperature.

Preparation of Chitosan oligosaccharide -g- Glycidyl methacrylate / Polypropylene glycol-Gluraralde hyde blend (COS – g – GMA / PPG-Glu)

About 1 g of Chitosan oligosaccharide -g- Glycidyl methacrylate copolymer was dispersed in a minimum amount of water and 1 g of polypropylene glycol was dissolved in a minimum amount of ethanol separately. The above solutions and 6mL of glutaraldehyde were then mixed thoroughly at room temperature in magnetic stirrer for 30 minutes. After stirring, COS – g – GMA / PPG-Glu blend was formed then poured into petri plates and dried at room temperature.

BATCH ADSORPTION STUDIES

Batch adsorption method was used in this study. Synthetic solution of Pb (II) ion taken in stoppered bottles and agitated with blend at room temperature in orbit shaker at fixed speed 210 rpm. The extent of heavy metal removal was investigated separately by changing adsorption dose, contact time of shaking and changing pH of the solution. After attaining the equilibrium adsorbent was separated by filtration using filter paper and aqueous phase concentration of metal was determined with atomic adsorption spectrophotometer. (Varian AA 240).

Effect of pH

The effect of pH on the adsorption of Pb (II) ion is presented in figure 1. The role of hydrogen ion concentration was examined in solutions at different pH 3–8 [6]. The pH of the solution affects the surface charge of the adsorbents [7]. The adsorbate speciation depends on the pH of the metal solution, the active sites on an adsorbent can either be protonated or deprotonated, and therefore the adsorption of other ions is affected [8]. At lower pH, less metal ion uptake is observed due to the competitive adsorption H+ and Pb2+ ions on COS-g-GMA/PPG-Glu blend surface. Protonation at low pH values reduces the number of binding sites for the metal ion.

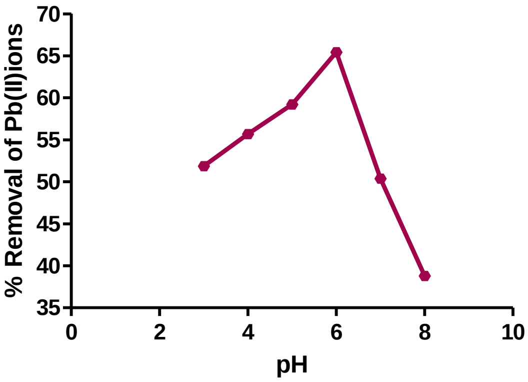

Figure-1 Effect of pH on the adsorption of Pb(II) ions onto COS-g-GMA/PPG-Glu blend

In addition, the protonation of amino groups induces an electrostatic repulsion on metal cations, hence reduces available sites for metallic ions [9]. However, Pb(II) ions uptake increases as the pH increases, while most active sites on the adsorbent are de-protonated resulting to the more net attractive force which is responsible for high lead metal ion adsorption from aqueous solution. The optimum adsorption takes place at pH 6. Further increase in pH leads to the precipitation of lead hydroxide complexes, which inhibits the adsorption process.

Effect of adsorbent dose

The addiction of the metal ion removal on adsorbent dose was investigated by varying the amount of COS-g-GMA/PPG-Glu blend from 1 to 6 g, even as maintaining other parameters as constant. The effect of adsorbent dose on the adsorption of Pb2+ ions were shown in Figure. 2. From Figure. 2, it was noticeable that the removal percentage of lead (II) ion increases with increasing the adsorbent dose from 1 g to 5 g. The initial increase in the metal ion removal percentage was due to the greater availability of the exchangeable sites or exterior area at higher concentration provided by the adsorbent necessary for the adsorption to occur [10].

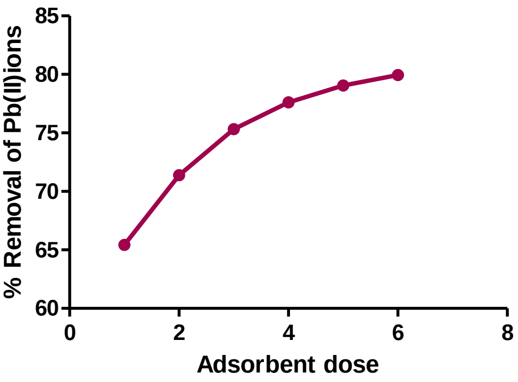

Figure-2 Effect of adsorbent dose on the adsorption of Pb(II) ions onto COS-g-GMA/PPG-Glu blend

Further addition of the adsorbent beyond this 5 g does not cause that much considerable change in the adsorption. This may be due to the overlapping/diffusion of adsorption sites as a result of overloading of adsorbent particles [11]. Another reason may be the inter-particle interaction, such as aggregation, resulting from high adsorbent dose which will lead to a reduce in the total surface area of the adsorbent and also an increase in diffusional path length [12]. The maximum percentage removal of Pb (II) ions was about 79% at the dosage of 5 g. From the above observed results it was recognized that the optimum adsorbent dosage for removing Pb^{2+} ion was found to be 5 g.

Effect of contact time

Equilibrium time is one of the important parameters essential in batch adsorption process and therefore the effect of contact time on removal of lead (II) ion by COS-g-GMA/PPG-Glu blend was studied from 60 to 360 minutes and the observed results were shown in Figure-3.

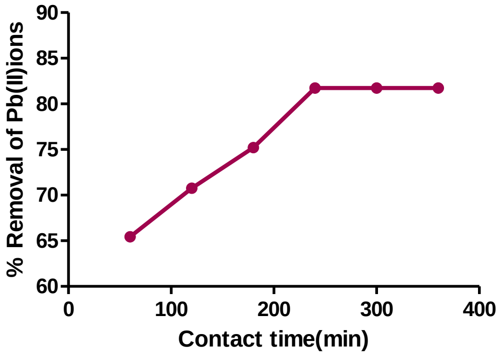

Figure-3 Effect of contact time on the adsorption of Pb(II) ions onto COS-g-GMA/PPG-Glu blend

From the results, it was identified that the percentage removal of lead (II) metal ions increased with increase of contact time. For the first 60 minutes, the percentage removal by the adsorbent was rapid. This may be because of the increased amount of time which leads the metal ions to make an effective contact with the blend and also due to the large surface area of the adsorbent [13]. After certain time, equilibrium was reached and hence there was no change in the uptake of metal ions due to decrease in the availability of active sites on the surface of sorbent.

Effect of initial metal ion concentration

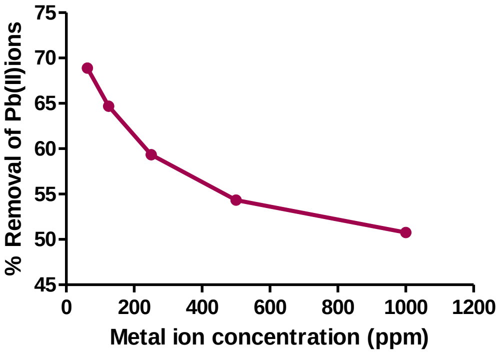

Figure-4 Effect of metal ion concentration on the adsorption of Pb (II) ions onto COS-g-GMA/PPG-Glu blend

The initial metal ion concentration is main feature in determining the adsorption effectiveness of a adsorbent. In the present study, the initial Pb^{2+} concentration is assorted from 62.5 mg/L to 1000 mg/L, at the same time as maintaining the other parameters as constant. From the result, It can be observed that the metal ions would interact with the binding sites very effectively to the higher percentage removal of Pb^{2+} ion whereas at higher metal ion concentration due to the saturation of adsorption sites the lower percentage removal was observed [14].

Adsorption isotherms

The isotherm models explain the relationship between the adsorbed metal ion concentration and concentration of the solution at equilibrium. For adsorption studies Langmuir and Freundlich equations are widely used [15,16].

Langmuir sorption isotherm

The linearized Langmuir isotherm allows the calculation of adsorption capacities and Langmuir constant by the following equation:

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

$C_{max} = KL / b$

where, C_{ads} = amount of metal ion adsorbed ($mg.\ g^{-1}$)

C_{eq} = equilibrium concentration of remaining metal ion in solu-tion ($mg.dm^{-3}$)

K_L = Langmuir constant ($dm^3 .g^{-1}$)

b = Langmuir constant ($dm^3 .mg^{-1}$)

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

A plot of C_{eq} / C_{ads} vs C_{eq} confirming the applicability of the Langmuir adsorption isotherm.

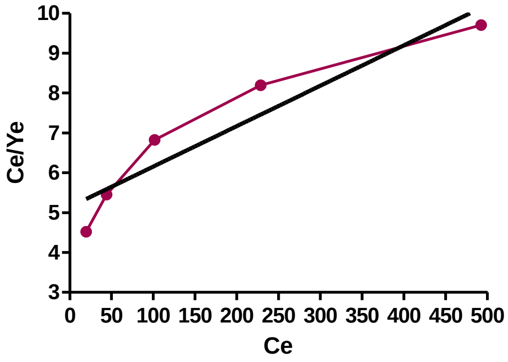

Figure -5 Langmuir plot for the adsorption of Pb (II) ion onto COS-g-GMA/PPG-Glu blend

The Langmuir equation was used to explain the data obtained from the adsorption of Pb (II) ions by graft copolymer adsorbent over the entire concentration range. A plot of C_{eq}/C_{ads} against C_{eq} gives a straight line

(Figure-5) The outcome of the adsorption isotherm shows a good correlation by the graft copolymer. Value of R^2(0.8933) shows correlation or linear relationship. The important features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L that is used to predict if an adsorption system is favorable or unfavourable[17]**.** The R_L values are in the range of $0 < R_L < 1$, it indicates that the adsorption of Pb (II)ions onto COS-g-GMA/PPG-glu blend is favourable.

Freundlich isotherm

The linearised form of Freundlich isotherm is given by the equation

$\text{Log } q_e = \log K_f + 1/n \text{ Log } C_e$

C_e = Equilibrium concentration of adsorbate in solution after adsorption (mg dm^3)

K_f = Emprical Freundlich constant or capacity factor (mg g^{-1})

1/n = Freundlich exponent or Freundlich intensity factor

Non-linear behaviour of adsorption indicates that adsorption energy barrier increases exponentially with increasing fraction of filled sites on the adsorbent. K_f and n are Freundlich constants. K_f indicates the relative sorption capacity and n is the measure of the nature and strength of the sorption process and the distribution of active sites. Figure-6 corresponds to the Freundlich isotherm of lead (II)ions. Mathematical calculations showed that n values are between 1 and 10 representing beneficial sorption [18]

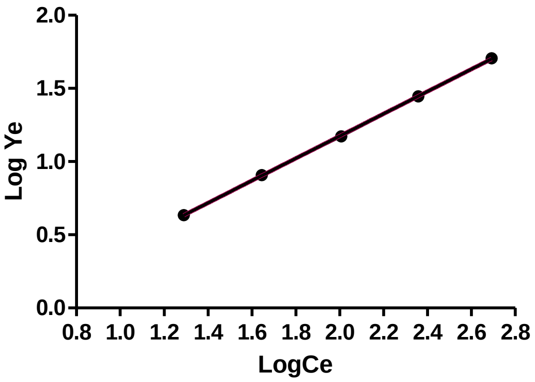

Figure-6 Freundlich plot for the adsorption of Pb (II) ion onto COS-g-GMA/PPG-Glu blend

The comparison of R^2 values of both the isotherms reveals that the R^2(0.9999) values of the Freundlich isotherm was found to be higher than the R^2(0.8933) values for the Langmuir isotherm. From the observed results, it was concluded that the experimental value is better fitted with the Freundlich adsorption isotherm model when compared to the Langmuir adsorption isotherm model and hence it was evident that the adsorption of lead(II) ions onto COS-g-GMA/PPG-Glu blend follows multilayer adsorption on the surface than monolayer adsorption.

Kinetic sorption mechanisms

Pseudo first order model

The initial concentration of solute is high, then adsorption process obeys pseudo first order model. The lineralized form of pseudo first order equation is given as follows

$\text{Log}(q_e - q_t) = \log q_e - k_1 t/2.303$ (19)

where q_e and q_t are the amounts of metal adsorbed (mg/g) at equilibrium and at time t (min) and k_1 (min^{-1}) is the adsorption rate constant of pseudo-first-order adsorption respectively.

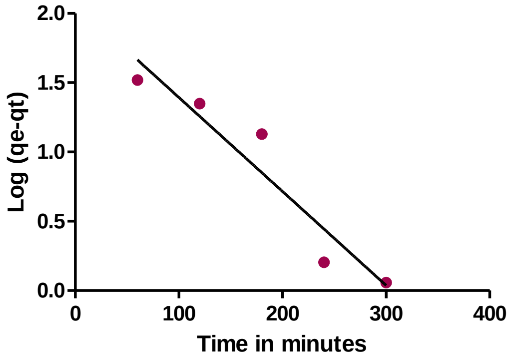

Figure-7 Pseudo first order plot for the adsorption of Pb(II) ion onto COS-g-GMA/PPG-Glu blend

A linear plot of log ($q_e - q_t$) against time allows one to obtain the rate constant. The pseudo first order kinetic plot for the sorption of Pb (II) ion from aqueous solution onto COS-g-GMA/PPG-glu blend was represented in Fig.7. From the slope and intercept of the linear plot of log ($q_e - q_t$) against time, the pseudo first order rate constant k_1 and the equilibrium adsorption capacity q_e and R^2 (0.9095) was calculated.

Pseudo second order model

The pseudo-second-order rate equation can be represented as follows

$\text{Log}(q_e - q_t) = \log q_e - k_1 t/2.303$ (19)

where q_e and q_t are the amounts of metal adsorbed (mg/g) at equilibrium and at time t (min), and k_2 (g mg^{-1} min^{-1}) is the adsorption rate constant of pseudo second order adsorption rate respectively. A linear plot of (t/q_t) versus t drawn for the pseudo-second-order model was represented in figure 8. The slope and intercept of the linear plot of t/q_t versus time gives the values of K_F and n respectively.

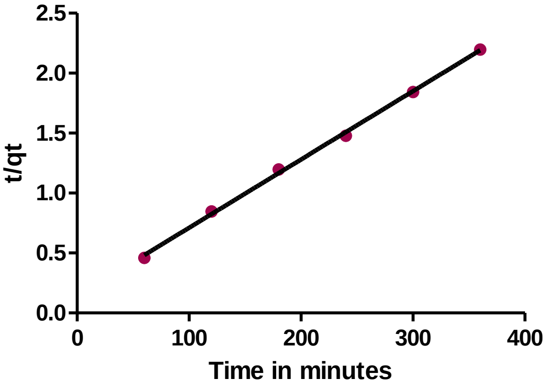

Figure-8 Pseudo second order plot for the adsorption of Pb (II) onto COS-g-GMA/PPG-Glu blend

The rate constants k_1 and k_2 can be obtained from the plot of experimental data. The pseudo-second-order equations show a good correlation of the experimental results with the linearized form (R^2-0.9986). The results elucidate that the kinetic behavior of lead sorption by COS-g-GMA/PPG-glu blend has been satisfactorily explaining with the pseudo-second-order sorption equation .

FT-IR Studies

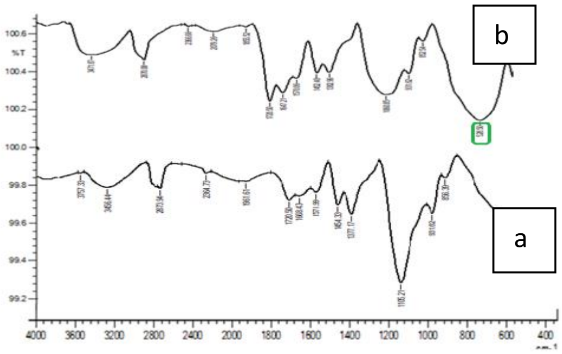

Figure -9: FT-IR spectrum of (a) COS-g-GMA/PPG-Glu blend (b) Pb (II) loaded COS-g-GMA/PPG-Glu blend

The FT-IR spectral details of COS-g-GMA/PPG-Glu blend before cadmium (II)ion adsorption shows a broad band around 3757 and 3456cm^{-1} attributed to -NH and -OH stretching vibration and a weak band at 2873 cm^{-1} for CH stretching. The characteristic absorption band at 1720 cm^{-1} was due to the C=O stretching vibration of glycidyl methacrylate. The absorption band at 1668 cm^{-1}, 1571 cm^{-1}, 1377 cm^{-1}, 1105 and 931 cm^{-1} were assigned to the amide I, amide II, C-H deformation vibrations, asymmetric stretching of the C-O-C Glycosidic linkage and NH bending. The absorption band at 856 cm^{-1} double bond of methacrylate.

On comparing FTIR spectrum of COD-g-GMA/PPG-Glu blend in metal loaded sample with above results, there is a significant shift in the band which suggest the participation of the functional groups such as OH, NH and C=O in metal ion elimination through chelation and dative bond formation between the metal and adsorbent.(20) The confirmation of metal ion attachment onto COS-g-GMA/PPG-Glu blend was evidenced from the appearance of band at 528 cm^{-1} corresponding to metal ligand stretching in metal loaded sample

CONCLUSION

This study appends to the sorption capacity of novel hybrid material of COS-g-GMA/PPG-Glu blend was evaluated for the sorption of Pb(II) ion from the aqueous solution. Based on Langmuir and Freundlich isotherm, the sorption capacity of COS-g-GMA/PPG-Glu blend was high and the adsorbent favored Freundlich isotherm i.e multilayer adsorption taken place effectively. The kinetics studies showed that the adsorption adhered to pseudo second order kinetics. Thus, the novel hybrid material of COS-g-GMA/PPG-Glu blend is found to be a very good biosorbent for the removal of lead (II)ions from aqueous solution.

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