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MODELING FIXED BED COLUMN FOR LEAD (II) REMOVAL FROM AQUEOUS SOLUTION USING NANOCHITOSAN/SODIUM ALGINATE/MICROCRYSTALLINE CELLULOSE BEADS

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ABSTRACT

Fixed-bed column studies were conducted to evaluate the performance of nanochitosan (NCS) /sodium alginate (SA) / microcrystalline cellulose (MC) beads for the removal of divalent lead ions [Pb(II)] from aqueous environments. Various factors such as the effect of flow rate, bed height and initial dye concentration on the adsorption process were investigated. The observed results of percentage removal of lead(II) determined from the breakthrough curves at different flow rates, initial metal ion concentration and bed heights showed that the column demonstrate fairly well performance at the higher bed height, lower influent lead (II) concentration and lower flow rate. The breakthrough time and exhaustion time were found to increase with increasing bed height and it shows a decrease with increasing flow rate and influent lead (II) concentration. Three kinetic models namely Thomas, Yoon Nelson and Adam Bohart model was used to analyze the experimental data and the model parameters were evaluated. The comparison of R^2 values reveals that both the Thomas and Yoon–Nelson models were found to have a better fit than the Adams–Bohart model. These results show that NCS/SA/MC bead can be successfully employed for the elimination of Pb(II) from aqueous solution.

KEYWORDS: Column, breakthrough time, exhaustion time, Lead (II), Kinetic models.

INTRODUCTION

On a global scale, recently the environmental pollution mainly arises due to the discharge of effluents containing various organic and inorganic pollutants (heavy metals) from a wide range of industrial applications, e.g., microelectronics, electroplating, battery manufacturing, metal finishing, mining and metallurgical products, dyestuffs, tanneries, chemicals, and pharmaceuticals.[1] Among the various pollutants present in industrial effluents, the heavy metals are considered to be priority pollutants (Cu, Pb, Cr, Fe, Ni, Cd etc.) even at very low concentrations to living organisms and this was due to their highly toxic nature and the carcinogenic properties.

In drinking water and industrial wastewater, when compared to the other toxic heavy metals, lead is the major environmental contaminant[2], which is originating from battery manufacturing waste, erosion of natural deposits, leather finishing, and metal plating.[3] Even in the ionic state, the heavy metal lead possesses more toxicity and due to its high toxic nature, it becomes an enzyme inhibitor in the cells when it accumulates in living tissues and it is therefore termed as metabolic poison. The major health problems of lead include, damage to kidney, liver, reproductive system, nervous system and the brain.[4][5] According to the environmental protection agency, the maximum allowable limits for lead in discharged wastewater is observed to be 0.05 mg L^{-1} respectively.[6][7]

In order to maintain a sustainable global ecosystem and also to comply with EPA guidelines, certain methods were introduced by many researchers for controlling and reducing the levels of toxic heavy metal ions in wastewater.[8] Many methods including adsorption, membrane separation, ion–exchange and electrolysis were employed by various researchers for this metal ions removal. But over the other methods, since the adsorption process of such heavy metal contaminants using variety of adsorbents is very cheap, effective and also easy to proceed for treatment purpose, the adsorption method is preferably chosen in this study.[9][10] Under continuous flow conditions, the fixed-bed adsorption has been proven to be an effective process for removing the toxic heavy metal ions and this was due to its operational simplicity, possibility of in situ generation, ease of operation and handling.[11][12]

Especially for purifying the liquid mixture such as the industrial waste effluents, the fixed bed adsorption has been widely used.[13] The comparison of column with batch adsorption studies reveals that the adsorption on packed bed columns presents several advantages such as simplicity in operation, high removal of metals and can be simply scaled up from a lab process.[14] Various adsorbents such as polymeric materials, minerals, industrial by-products, organic materials of biological origin, zeolites, agricultural wastes and biomass has been used for the removal of heavy metals from water.[15]

In recent years, there has been an increasing emphasis on the adsorbent with low cost for the heavy metal ions removal. In order to eliminate low levels of heavy metal ions from waste water stream, most effective adsorbents like the naturally occurring polysaccharides such as alginic acid and chitosan have been utilizied in their work by various researchers.[16] Chitosan, poly β (1→4)-2-amino-2-deoxy-D-glucose is obtained through deacetylation process of chitin using a strong alkaline solution. Among natural adsorbents, chitosan has been proven to have the highest metal chelating capacity[17] and certain chemical modifications to chitosan can be done in this study to introduce various functional groups like amines, amides, thiols, imines and phosphates since it helps in increasing the chitosan high selectivity and adsorption capacity.[18]

For many water pollution problems, nowadays, the nano techniques provide a ready solution[19][20] and in the field of nanotechnology, the ability of controlling nanoparticle size is highly desirable for most applications.[21] The adsorption capacity can be controlled by sorbent particle size.[22] and hence in this study, the nanochitosan (NCS) which is an environmentally friendly and bioactive material were produced and used for the removal of metal ions. The alginate biopolymer is a linear polysaccharide composed of alternating blocks of 1-4 linked α-L-guluronic and β-D-mannuronic acid fragments. The alginate biopolymer was proved to be excellent materials for water purification and this is because of their high affinity for chelation with polyvalent metal cations in particular with divalent metal ions.[23]

Due to the presence of various functional groups and the low-cost, the agricultural by-products acts as very interesting adsorbents for the removal of metal ions and dyes from wastewater.[24][25][26] Certain main components like lignin, cellulose and other functional groups, including carboxylic acids, phenols, carbonyls and ethers were present in the agricultural byproducts. The thermo chemical or chemical modifications done with cellulosic raw materials renders them more effective for the collection and binding of various metal ions. Steam explosion method is mainly used to isolate cellulose from hardwood and agricultural waste residues. In the present research work, the cellulose was extracted from the banana stem fiber in microcrystalline form by applying steam explosion process with banana stem fiber and then it is utilized in preparing the adsorbent. Based on the literature survey, in the present research work, three materials namely nanochitosan, sodium alginate and the microcrystalline cellulose extracted from banana fiber using steam explosion method has been employed in adsorbent preparation.

The main purpose of the present research work was to synthesize the ternary blended NCS/SA/MC mixture in the form of bead and to determine the potentiality of this ternary (NCS/SA/MC) bead to remove lead (II) from aqueous solution using fixed bed column studies. In this study, the strategic steps in the design and the fixed bed column operation used for the removal of metal contaminants from industrial wastewater were discussed in this study. The influences of bed height, flow rate and initial metal ion concentration on the adsorption performance of Pb (II) onto NCS/SA/MC bead in a fixed-bed column were investigated and the equilibrium data were finally analysed using Thomas, Yoon - Nelson and Adam Bohart kinetic models.

MATERIALS AND METHODS

Materials

The material used for this study mainly includes the banana fiber which was collected from local farms. Commercial grade sodium hydroxide was obtained from Central Drug House Pvt. Ltd. and certain chemicals such as sodium alginate, sodium hypochlorite and oxalic acid was purchased from Nice chemicals, Kerala, India. The crosslinking agent calcium chloride, sodium tripolyphosphate and the solvent glacial acetic acid were procured from Finar chemicals, Ahmedabad and Thomas Bakers chemicals Pvt. Ltd., Mumbai. All the above chemicals used in the present research work were of analytical grade.

Microcrystalline cellulose extraction from banana fiber

Bibin Mathew Cherian and his coworkers reported about the isolation of cellulose from the banana fiber using steam explosion method[27] as follows. In order to extract the microcrystalline cellulose from banana fiber, the combined chemical and mechanical treatments was done. For delignification process, initially the chopped lignocellulosic banana fibers (30g) was soaked in 2% NaOH (fiber to liquor ratio 1:10) solution and followed by this the steam explosion of alkaline treated fiber was carried out in an autoclave at a pressure of 20 lb for a period of 1 h. The obtained fibrils were then washed with distilled water prior to bleaching with sodium hypochlorite solution. The bleaching process was done under the autoclave for a period of 30 minutes and after this process is over, the bleached fibers was hydrolyzed with 11%oxalic acid and stirred vigorously. Finally the steamed alkali and acid treated fibers were stirred mechanically well to extract the cellulose completely with different degrees of crystallinity. The photograph of the microcrystalline cellulose extracted from banana fiber using steam explosion method was represented below (Fig.A).

Fig.A: Microcrystalline cellulose extracted from banana fiber using steam explosion method where a) steam exploded fiber b) bleached fiber c) acid treated fiberand d) mechanically treated fiber.

Preparation of nanochitosan

In order to the prepare the nanochitosan by ionotropic gelation method, initially a homogeneous viscous gel of chitosan were prepared by dissolving 1g of it in 200 ml of 2% acetic acid solution. This homogeneous chitosan gel was then ionically cross linked by the dropwise addition of sodium tripolyphosphate (TPP) solution (0.8 g of sodium tripolyphosphate dissolved in 107 ml of conductivity water). Upon mixing of the TPP solution to the chitosan solution, a milky coloured like suspension of nanochitosan was obtained and before sitting for an additional 24 h to reach the equilibrium, the above prepared mixture was stirred well for a period 30 minutes effectively. After this attainment of equilibrium, the supernatant solution was decanted. Followed by this, the thick suspension of nanochitosan settled at the bottom of the beaker was preserved in the refrigerator and then stored for further use.

Preparation of NCS/SA/MC (2:8:1) bead

Ternary NCS/SA/MC biopolymeric beads were prepared by mixing an aqueous 2.5% nanochitosan solution with aqueous 10 wt% alginate solution and aqueous 1.25 wt% microcrystalline cellulose solution. This solution mixture is stirred well for about 30 minutes at 500 rpm until a homogeneous viscous gel like texture is obtained. This ternary blended (NCS/SA/MC) homogeneous viscous gel like solution mixture was then poured as droplets into 100 ml of 0.2 M calcium chloride solution to perform effective cross linking process. The NCS/SA/MC beads so produced were then allowed to harden for 24 h, filtered, washed, and then dried to obtain the desired adsorbent. A photograph of the prepared NCS/SA/MC bead (Fig.B) was shown below:

Fig.B: Photograph of ternary nanochitosan/sodium alginate/microcrystalline celluose bead.

Fixed Bed Column Design and Experimental Procedure

Fixed bed column experiments were carried out in borosilicate glass column of 2.8 cm internal diameter and 30 cm height. This column was filled with different amount of NCS/SA/MC beads in order to achieve specific bed height respectively. In order to support the beads in the column and to minimize the effects of air bubble at the inlet and outlet regions of a packed column, 1.0 cm glass wool were kept at the bottom and the at top of the column respectively to ensure a closely packed arrangement. The metal ion solution of specific desired concentration was then fed through the column containing closely packed MCS/SA/MC bead in the down flow rate and the treated Pb(II) solution was then collected from the bottom with same flow rate of feed stream at specific time intervals. The Pb(II) concentration remaining after adsorption processwas then estimated using AAS studies. The operation of the column was stopped when effluent metal concentration (C_f) exceeded a value of 98% of the initial metal ion concentration (C_o). The schematic diagram of the packed bed column was shown below (Fig.C).

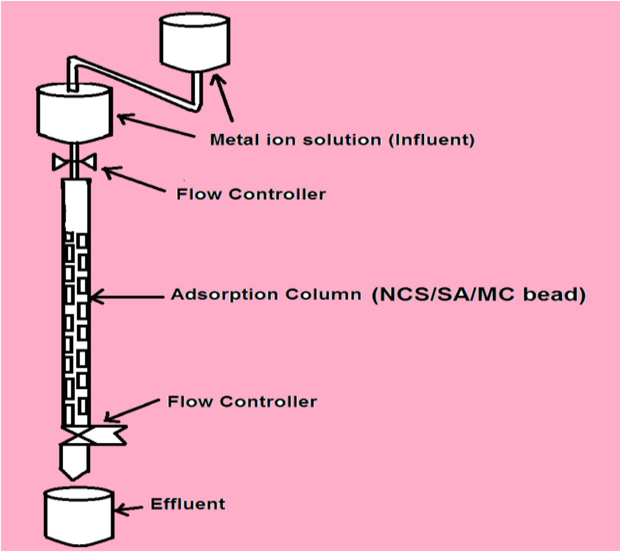

Fig.C: Fixed bed column packed with NCS/SA/MC bead.

In this study, various parameters on the column performance was investigated. (a) Effect of bed height: bed height was varied between 1.0 to 1.5 cm, keeping flow rate (1.5 ml/min) and initial metal ion concentration (200mg/L) constant (b) Effect of flow rate: flow rate was varied between 1.0 and 1.5 mL/min, while bed height (1.5 cm) and initial metal ion concentration (200 mg/L) were held constant (c) Effect of initial metal ion concentration: initial metal ion concentration was varied between 200mg/L and 300 mg/L at constant bed height (1.5 cm) and flow rate (1/0 ml/min).

Design Parameters of adsorption column

In order to analyze the dynamic removal of metal ion in fixed bed column, the breakthrough curves ((Effluent concentration (C_t) / Influent concentration (C_o) vs. time t) were drawn and the datas were evaluated with the help of following equations.

The area under the breakthrough curve (A) can be obtained by integrating the adsorbed concentration (Cad in mg/L) versus t (min) and it is used to find the total adsorbed Pb(II) quantity (maximum column capacity). The total adsorbed metal quantity ($q_{total,}$ mg) in the column for a given feed concentration and flow rate is calculated as follows

$$q_{total} = \frac{QA}{1000} = \frac{Q}{1000}\int_{t=0}^{t=total} C_{ad}.\,dt$$

Total amount of metal ion sent to column (m_{total}) is calculated as

$$m_{total} = \frac{C_0\,Q\,t_{total}}{1000}$$

Total removal is calculated as

$$\text{Total Removal } (\%) = \frac{q_{total}}{m_{total}} \text{ x } 100$$

The breakthrough capacity (q_b) and the volume of effluent solution (V_{eff}) treated was determined using the following equation

$$q_b = \frac{t_b Q C_o}{m}$$

$$V_{eff} = Q t_{total}$$

Where C_o = initial influent concentration of solute (mg/l), q_b = breakthrough adsorption capacity (mg/g), t_b = breakthrough time (min), Q = volumetric flow rate (ml/min), m = mass of NCS/SA/MC film used (g), V_{eff} = volume of effluent (L), t_{total} = total flow time respectively.

Column breakthrough curve modeling

Simple mathematical kinetic models such as Thomas model, Yoon Nelson model and Adam Bohart models have been developed by many researchers for the successful design and operation of laboratory-scale fixed bed column adsorption. Breakthrough curves yielded for flow rate, initial concentration, and bed height were predicted using these kinetic models.

RESULTS AND DISCUSSION

Effect of bed height

In this study, removal of Pb(II) in the adsorption process was studied using NCS/SA/MC bead adsorbent under the different bed heights (1.0cm and 1.5 cm) by keeping flow rate and inlet concentration of Pb(II) constant at 1.5 (ml/min) and 200 (mg/L), respectively. Fig.1 represents the breakthrough curves for different bed heights of 1.0 cm and 1.5 cm.

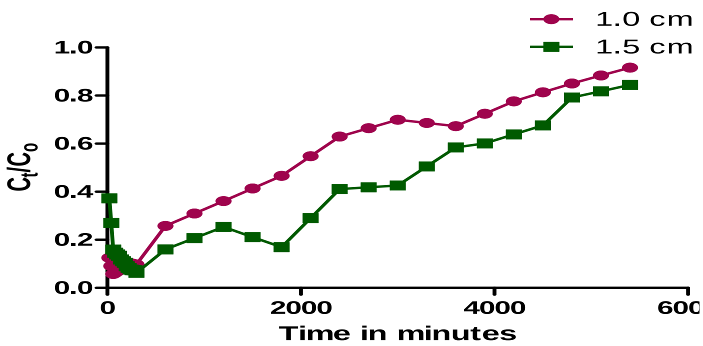

Fig.1: Effect of bed heights on the break through profile of adsorption of lead(II) by NCS/SA/MC bead.

The obtained results showed that the breakthrough curves were steeper with lower bed height. As the bed height is increased, the breakthrough time, removal efficiency and saturation time increased. With an increase in mass of adsorbent from 2.5 g (1.0 cm bed height) to 4 g (1.5 cm bed height), the total percentage removal of Pb(II) for the fixed-bed adsorption column showed an increase of % metal ion removal from 51.60% to 64.70%. The increased metal ion removal percentage with increase in bed height might be due to the increase in the surface area of adsorbent, which provided higher number of available adsorption sites and the increase in volume influent.[28][29] The breakthrough time was found to be increased from 240 min to 300 min with increase in bed height from 1.0cm to1.5 cm and the possible reason behind this increasing breakthrough time with increasing bed height is due to the availability of more time for the metal ion to contact with the adsorbent resulting in delayed breakthrough and as well as the saturation leading to an increase in the volume of solution treated.[30]

Effect of flow rate

Volumetric flow rate is one of the main factors which drastically influence the adsorption behavior of a system in a continuous flow mode. In order to utilize the bed for its maximum capacity with minimal flow rate, the influence of flow rate should be studied and this will be helpful for the large scale treatment systems.[31] Fig.2 shows the effect of flow rate for the adsorption of lead (II) onto NCS/SA/MC bead at flow rates of 1.0 ml/min and 1.5 ml/min kept at constant influent concentration of 200 mg/L and bed height of 1.5 cm respectively.

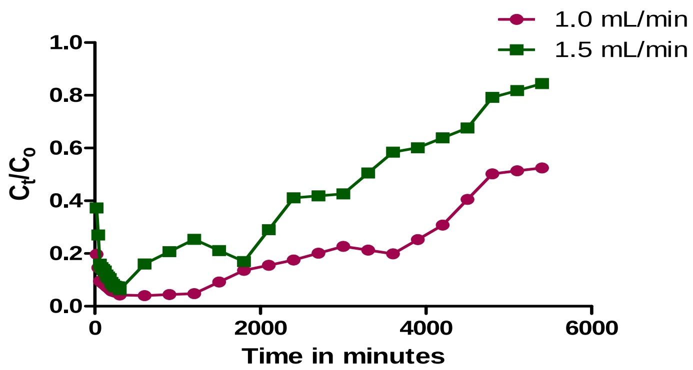

Fig.2: Effect of flow rate on the break through profile of adsorption of lead (II) by NCS/SA/MC bead.

The results presented in the figure-2 showed that when compared to the higher flow rate (1.5ml/min), the column performed well with higher removal efficiency, longer breakthrough time and longer saturation time at the lower flow rate (1.0 ml/min). At higher flow rate, the decreased Pb(II) removal efficiency was mainly due to the decrease in residence time and higher intraparticle diffusion effect of the aqueous solution in the fixed-bed. At higher flow rate, due to the reduced contact time, there is less time for lateral diffusion to occur within the NCS/SA/MC bead bed due to weak distribution of the liquid inside the fixed-bed, and as a result of this lower diffusivity of the solute among the adsorbent particles[32], it showed a decreased Pb(II) percentage removal. In other words we can say that at higher flow rate the contact time of the metal ions with the adsorbent in the column is not enough to reach adsorption equilibrium and hence the metal ion (Pb(II)) solution leaves the column before equilibrium occurs and this causes a reduction in the removal efficiency, breakthrough time and saturation time.[33] Based on the above obtained results it was evident that the optimal flow rate was found to be 1.0 ml/min for Pb(II) removal from aqueous solution.

Effect of initial metal ion concentration

The breakthrough curves obtained for different initial metal concentrations (200–300 mg L^{-1}) at a constant flow rate (1.0 mL min^{-1}) and a bed height of 1.5 cm was represented in Fig. 3.

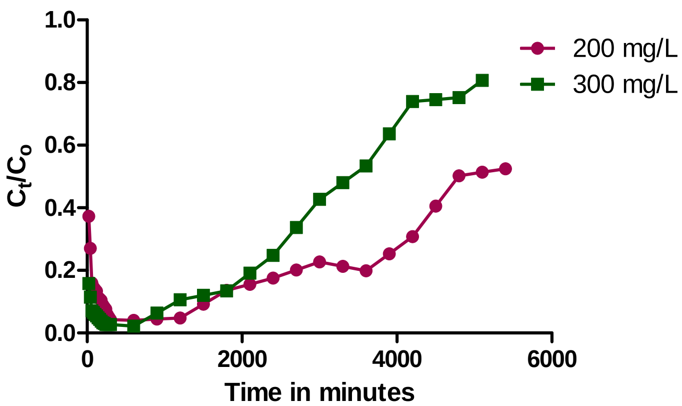

Fig.3: Effect of initial metal ion concentration on the breakthrough profile of adsorption of lead(II) by NCS/SA/MC bead.

The effect of initial concentration of Pb (II) ions on their adsorption process was studied at various initial metal ion concentrations onto NCS/SA/MC bead and from the observed results (presented in Fig.3) it was evident that, the increasing initial metal concentration from 200 to 300 mg L^{-1} decreased the breakthrough time and exhaustion time respectively. The breakthrough time shows a decrease from 360min to 300 min with the increase in initial Pb(II) concentration from 200 to 300 mg/L and the saturation time was found to be decreased from 5400 min to 4200 min with an increase in the initial Pb(II) concentration from 200 to

300 mg/L. A similar decrease of percentage removal was observed from 77.32% to 70.95% for the adsorption of Pb^{2+} onto NCS/SA/MC bead with the increase in initial metal ion concentration from 200 to 300 mg/L.

The above observed decline in breakthrough time with increased initial metal concentration was mainly attributed to the slower mass transport caused by the reduced metal concentration gradient, which consequently decreased the diffusion or mass transfer coefficient. Higher metal ion concentration has been shown to lead to a higher driving force for the metal ions to overcome the mass transfer resistance in the liquid phase and hence as a result with the increasing inlet metal concentration, the quick saturation of the available binding sites for metal ions happens leading to the decrease in breakthrough time.[34] At lower metal ion concentration, when compared to the available metal ions, the available active sites for metal ion attachment was found to be greater and hence due to this availability of sufficient active sites for the adsorption of the metal ions, percentage removal of metal ions is greater at lower initial metal ion concentration.[35] The decreased percentage removal at higher metal ion concentration is due to the exhaustive saturation of active sites for metal ion attachment.[36]

Modelling Studies for the Removal of Pb (II) in a Packed Bed Column

In order to describe the dynamic adsorption behavior of Pb(II) onto NCS/SA/MC bead in the continuous column adsorption process, three kinetic models namely Thomas, Yoon Nelson and Adam Bohart model were utilized in this study.

Thomas Kinetic Model

The plug flow behavior of fixed bed can be explained using Thomas model. This Thomas model follows pseudo second order reversible reaction kinetics and is mainly based on the Langmuir adsorption isotherm for equilibrium systems.[37] The adsorption rate constant and the solid phase concentration of the metal ion on the adsorbent from the continuous mode studies can be calculated with the help of Thomas kinetic model.[38] The linearized form of the Thomas model[39] can be expressed as

$$\ln\left(\frac{C_o}{C_t}-1\right)=\frac{k_{TH}q_oX}{Q}-\frac{k_{TH}C_o}{Q}V_{eff}$$

Where

C_t is the effluent metal ion concentration at time t (mg/L),

C_o is the influent metal ion concentration (mg/L),

q_o is the maximum adsorption capacity (mg g^{-1}),

V_{eff} is the effluent volume (L)

k_{TH} is the thomas rate constant (mL min^{-1} mg^{-1}),

X is the amount of adsorbent in the column (g) and

Q is the flow rate (mL min^{-1}).

Using linear regression analysis, with the help of the slope and intercept of Thomas kinetic plot of ln(C_o/C_t -1) against effluent volume (V_{eff}), the kinetic coefficient k_{TH}, and the equilibrium uptake per gram of the adsorbent q_o can be determined. Thomas model is suitable for adsorption processes where the external and internal diffusions will not be the limiting. The Thomas linear kinetic plot of ln(C_o/C_t -1) Vs Effluent volume (V_{eff}) using experimental data at different bed heights (1cm, 1.5 cm), flow rates (1ml/min, 1.5 ml/min) and initial metal ion concentrations (200mg/L, 300mg/L) for NCS/SA/MC film was represented in Fig.4-6. Calculated values of Thomas model parameters and the R^2 at different conditions using linear regression analysis for NCS/SA/MC bead was shown in Table-1.

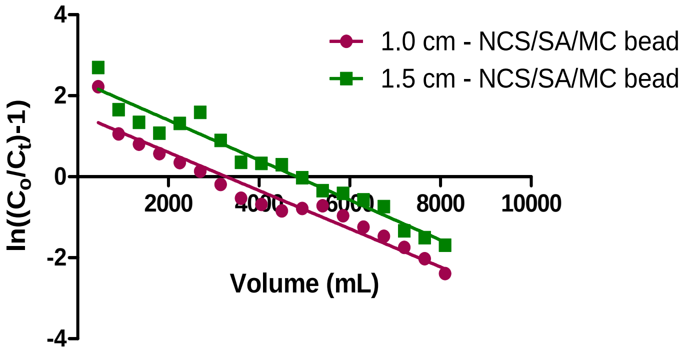

Fig. 4: Effect of bed height- Thomas kinetic plot for the adsorption of lead(II) onto NCS/SA/MC bead.

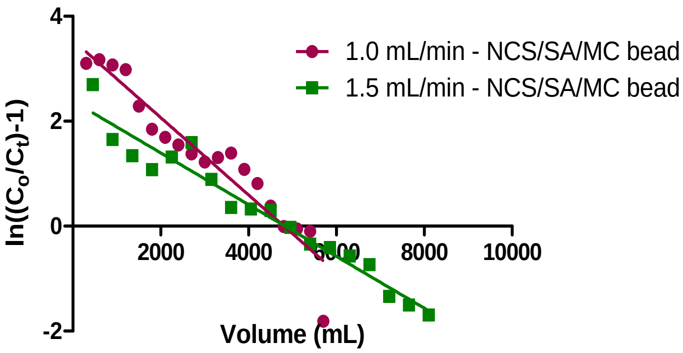

Fig.5: Effect of flow rate- Thomas kinetic plot for the adsorption of lead (II) onto NCS/SA/MC bead.

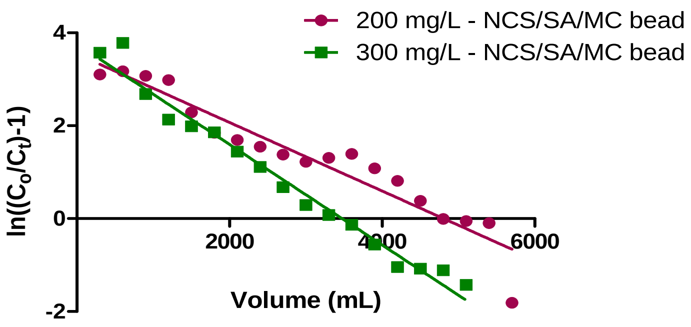

Fig.6: Effect of initial metal ion concentration- Thomas kinetic plot for the adsorption of lead(II) onto NCS/SA/MC bead.

Table-1: Thomas model parameters at different conditions using linear regression analysis for NCS/SA/MC bead.

Sample	Inlet conc (mg/L)	bed height (cm)	Flow rate (ml/min)	Constant		
				k_{TH} (ml/min/mg) ($x10^{-6}$)	q_0(mg/g) ($x10^4$)	R^2
NCS/SA/MC bead	200	**1.0**	1.5	3.537	26.2256	0.9370
	200	**1.5**	1.5	3.698	24.1635	0.9524
	200	1.5	**1.0**	3.688	24.0339	0.9140
	200	1.5	**1.5**	3.698	24.1635	0.9524
	200	1.5	1.0	3.688	24.0339	0.9140
	300	1.5	1.0	3.607	26.0559	0.9774

The dependence of Thomas rate constant, k_{TH} on flow rate, initial ion concentration and bed height was identified from the results of k_{TH}, R^2 and q_o presented in Table-(1) obtained from Fig.4-6. The slope of the curve is related to the rate of transfer of metal ions from solution to the adsorbent and this was characterized from the thomas rate constant (k_{TH}). With increasing flow rate, the maximum adsorption capacity q_o shows an increase but it shows a decrease with increasing bed height. At higher flow rate, due to the availability of active sites of the adsorbents by the numerous adsorbate molecules present in higher flow of solution, the maximum adsorption capacity q_o was found to be increased with increasing flow rate.[40]

As the concentration is increased, the value of q_o increased, whereas the value of k_{TH} q_o showed a reverse trend i.e., decreased with increase in concentration. The kinetic data were fitted well to Thomas model and this was concluded from the observed higher correlation coefficient value. The fitting of experimental data with the Thomas model indicate that the external and internal diffusions were not the rate limiting step and no axial dispersion is present.

Yoon –Nelson kinetic model

A relatively simple model has been developed by Yoon Nelson and it was mainly utilized to describe the adsorption behavior in the continuous column adsorption.[41] When compared to the other kinetic models this Yoon nelson model is less complicated and also requires no detailed data concerning the type of adsorbent, characteristics of adsorbate and the physical properties of the adsorption bed.[42] Yoon Nelson model presumes that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of the adsorbate adsorption and the adsorbate breakthrough on the adsorbent.[43] The linearized form of the Yoon-Nelson model is given below

$$\ln\left(\frac{C_t}{C_o - C_t}\right) = k_{YN}\, t - \tau k_{YN}$$

Where,

k_{YN} is Yoon and Nelson rate constant (min^{-1}),

C_t, C_o is the effluent and inlet solute concentrations,

Ʈ is the time required for 50% adsorbate breakthrough (min) and

T is the breakthrough (sampling) time (min).

The Yoon Nelson kinetic plot for the adsorption of lead(II) onto NCS/SA/MC bead studied at different bed heights, flow rate and initial metal ion concentration was represented in Fig.7-9. The slope and intercept of the plot of ln (C_t/C_o-C_t) versus t gives a straight line and with the help of slope (k_{YN}) and intercept (-Ʈ.k_{YN}) the kinetic parameters k_{YN} and Ʈ values were calculated.

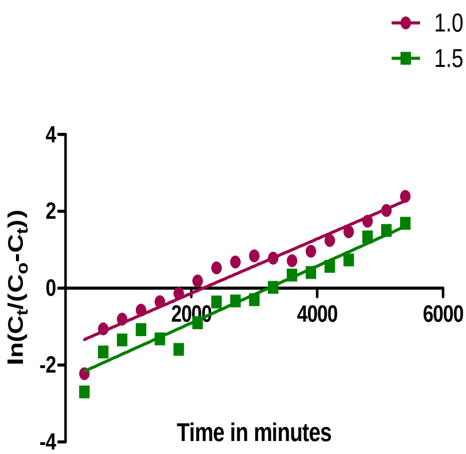

Fig. 7: Effect of bed height- Yoon Nelson kinetic plot for the adsorption of lead(II) onto NCS/SA/MC bead.

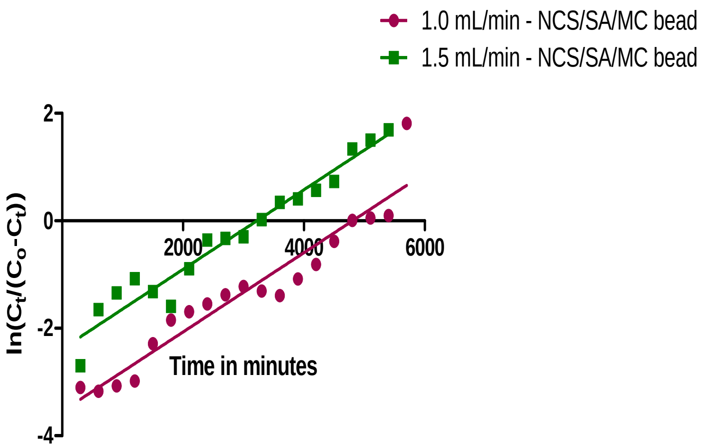

Fig.8: Effect of flow rate- Yoon Nelson kinetic plot for the adsorption of lead(II) onto NCS/SA/MC bead.

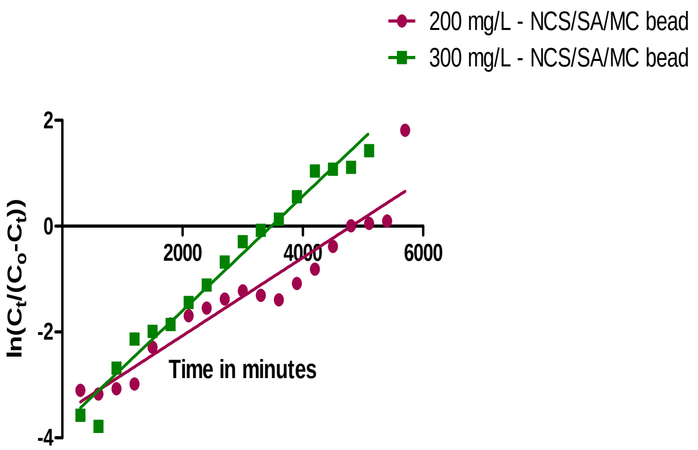

Fig.9: Effect of initial metal ion concentration- Yoon Nelson kinetic plot for the adsorption of lead (II) onto NCS/SA/MC bead.

Table: 2: Yoon Nelson model parameters at different conditions using linear regression analysis for NCS/SA/MC bead.

Sample	Inlet conc (mg/L)	bed height (cm)	Flow rate (ml/min)	Constant		
				k_{YN} (ml/min/mg) (X 10^{-3})	Ʈ (min)	R^2
NCS/SA/MC bead	200	**1.0**	1.5	0.707	2185.468	0.9370
	200	**1.5**	1.5	0.740	3221.576	0.9524
	200	1.5	**1.0**	0.738	4806.780	0.9140
	200	1.5	**1.5**	0.740	3221.576	0.9524
	200	1.5	1.0	0.738	4806.780	0.9140
	300	1.5	1.0	1.082	3474.122	0.9774

The calculated values of Yoon nelson parameters and the correlation coefficients obtained at different conditions using linear regression analysis for NCS/SA/MC bead was represented in

Table-2. Results presented in Table-2 showed that the time required for 50% breakthrough τ decreased with increase in flow rate, initial metal ion concentration but it shows an increase with increase in bed height. In addition the obtained results also indicate that the Yoon Nelson rate constant (k_{YN}) increased with increased metal ion concentration, flow rate and bed height.

The increased metal ion uptake rate (k_{YN}) at higher metal ion concentration was attributed to the increased competition between adsorbate molecules for the adsorption sites with increasing metal ion concentration. The observed increased rate at higher flow rate is due to the increased passage of more number of metal ions through the adsorbent.[44] With increased flow rate and initial metal ion concentration, the τ value shows a decreased value and this might be due to the less residence time and quick attainment of saturation of colum.[45] Similarly, the increased τ value at higher bed height was due to slower saturation of column.

From the results presented in Table-1 and Table-2, it was evident that the correlation coefficients were found to be between 0.9370- 0.9774 and this observed higher correlation coefficient value indicate that better fit of both Thomas and Yoon Nelson model with the experimental data to a considerable extent.

Adam Bohart model

Based on the surface reaction theory, the Adams-Bohart model has been developed. This Adam Bohart model is based on the assumption that the adsorption rate is proportional to the fraction of adsorption capacity that still remains on the surface of the adsorbent.[46][47] This model predicts that the equilibrium is not instantaneous and therefore the rate of adsorption is directly proportional to the concentration of the adsorbate and the remaining capacity of the adsorbent.[48] The mathematical equation of this model can be expressed as follows

$$\ln\left(\frac{C_t}{C_o}\right) = k_{AB} C_o t - k_{AB} N_o \frac{Z}{F}$$

Where C_t and C_o are the effluent and influent concentrations (mg L^{-1}) at time t and zero,

k_{AB} is the kinetic constant (mL mg^{-1} min^{-1}),

t is time (min);

N_0 is the saturation concentration (mg L^{-1}),

Z is the bed depth of column (cm),

F is the superficial velocity of influent solution

The superficial velocity of influent solution can be calculated by dividing the flow rate by the column section area (cm/min). From the intercept and slope of linear plot of ln (C_t/C_o) against time (t), the kinetic parameters describing the characteristic operations of the column (k_{AB} and N_0) were determined.

The linear plot of Adam Bohart model with experimental data studied at different bed heights, initial metal ion concentrations and flow rates for NCS/SA/MC bead (lead (II)) was shown in Fig.10-12. The respective values of N_0, and k_{AB} calculated for all the breakthrough curves were summarized in Table-3 together with the corresponding correlation coefficients.

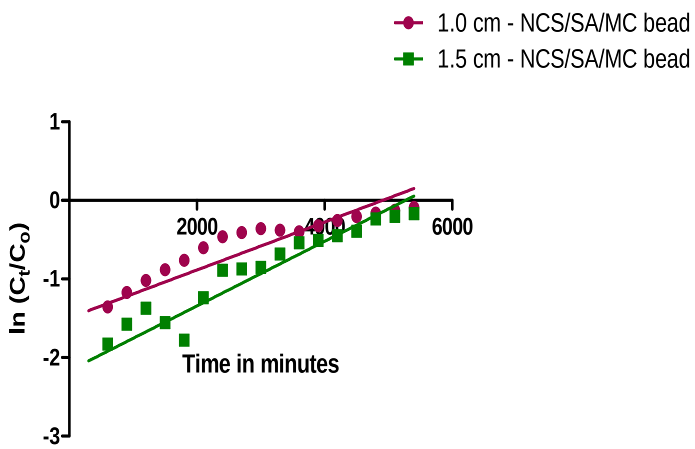

Fig.10: Effect of bed height- Adam Bohart kinetic plot for the adsorption of lead(II) onto NCS/SA/MC bead.

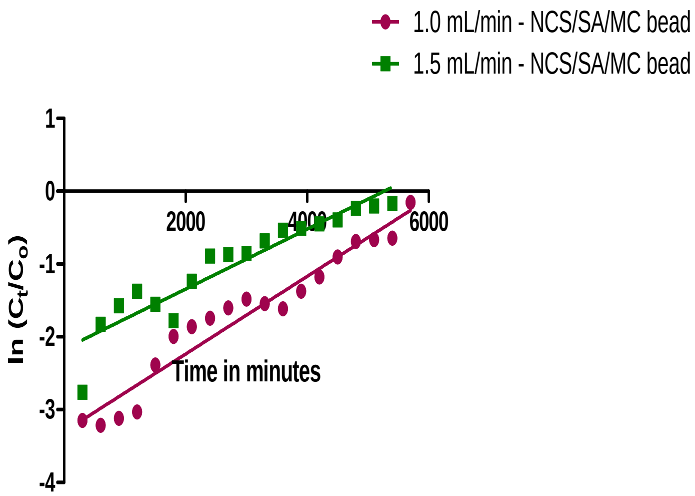

Fig.11: Effect of flow rate- Adam Bohart kinetic plot for the adsorption of lead(II) onto NCS/SA/MC bead.

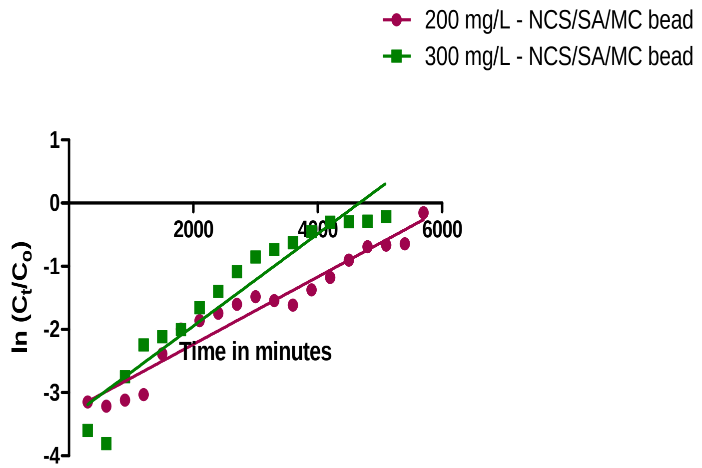

Fig.12: Effect of initial metal ion concentration- Adam Bohart kinetic plot for the adsorption of lead (II) onto NCS/SA/MC bead

Table-3: Adam Bohart model parameters at different conditions using linear regression analysis for NCS/SA/MC bead.

Sample	Inlet conc (mg/L)	bed height (cm)	Flow rate (ml/min)	Constant		
				k_{AB} (L/min/mg) (x 10^{-6})	N_o (mg/L) ($X10^4$)	R^2
NCS/SA/MC bead	200	**1.0**	1.5	1.524	16.7401	0.7535
	200	**1.5**	1.5	2.058	11.9791	0.8772
	200	1.5	**1.0**	2.666	9.3955	0.9436
	200	1.5	**1.5**	2.058	11.9791	0.8772
	200	1.5	1.0	2.666	9.3955	0.9436
	300	1.5	1.0	2.433	10.6190	0.9102

By applying the experimental data, the initial part of the breakthrough curve was described using the Adams–Bohart adsorption model and from the observed results presented in Table-3, it can be seen that the values of k_{AB} decreased with increase in initial metal ion concentration and as well as the flow rate. Conversely, the values of N_o increased with increase in flow rate and metal ion concentration but decreased with increase in bed height. The reason behind the fact is that, particularly in the initial part of adsorption in the column, the overall system kinetics may have been influenced by external mass transfer[49][50] and as a result it shows certain changes in the kinetic parameters. Since the obtained correlation coefficients (R^2) for this model was found to be low, it can be confirmed that the equilibrium data does not fit into the model perfectly. From this observed result it was concluded that the Adam's – Bohart model is unsuitable to explain the overall adsorption kinetics in the column.

CONCLUSION

A novel NCS/SA/MC bead can be synthesized and utilized as an adsorbent in a continuous column to remove lead(II) from aqueous solution. Based on the results obtained, it was concluded that the influence of bed height, flow rate and inlet metal ion concentration have a significant effect on Pb(II) adsorption by NCS/SA/MC bead. Results indicate that both breakthrough time and exhaustion time increases with increasing bed height, but decreases with increasing Pb(II) inlet concentration and flow rate. The optimal flow rate was observed to be 1.0 mL/min with a packing height of 1.5 cm and initial metal ion concentration of 200 mg/L for removing 78% Pb(II) from the aqueous solution. Finally based on the kinetic studies, it was concluded that when compared to the Adam Bohart kinetic model, the Thomas and Yoon-Nelson adsorption model was found to be a better fit with higher correlation coefficient values (R^2>0.96) which is used to describe the behavior of the adsorption of Pb(II) from aqueous solution in a continuous column using NCS/SA/MC bead.

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