6.1 INTRODUCTION

Lead is one of the most toxic heavy metals because it could act as the root of wide variety of the health trouble, such as nausea, renal failure, convulsions, cancer and even coma. It also alters the metabolism processes and subtle effects on intelligence [Jouad *et al*. (2005)]. For the application of adsorbent in industrial scale, the adsorption study by fixed bed column is more preferable [Kundu and Gupta (2005)]. The literature survey indicated that most of the reports involving lead removal by nanoparticles include batch mode study and only few report have been published on the fixed bed column studies [Zhang *et al.* (2008), Su *et al.* (2009), Saadi *et al*. (2013), Soltani *et al*., (2014), Sounthararajah *et al*. (2015)]. For this reason, an attemp has been made to remove lead from contaminated water using fixed bed up flow continuous column method. The main column design parameters such as bed depth, initial concentration of the lead ions, and flow rates have been studied. The optimization of various column parameters provides important information which helps in the designing the large scale adsorption column for industrial purpose. The breakthrough performance of the lead was analyzed by different well-established models such as Bed Depth Service Time (BDST), Thomas model, and Yoon-Nelson model. Desorption and regeneration studies of adsorbed lead and the exhausted column were also carried out. In this adsorption system, the GO/MgO nanocomposite used as adsorbent. The synthesis method of the GO/MgO nanocomposite is given in chapter 5.

6.2 MATERIAL AND METHOD

The column adsorption studies were performed in up-flow fixed-bed column made up of graduated borosilicate glass column (length 30 cm and internal diameter 1 cm). The column was packed with required amount of GO/MgO for the removal of lead from water. The column was operated at three different bed height i.e. 2.5, 5, 7.5 cm and flow rates 1.66, 3.32, and 4.98 mL/min. In addition to it the column experiments were also conducted at different lead concentrations (40. 60, and 80 mg/L). The effluent was collected from the upper end of the column at fixed interval of time and the residual lead ion concentration was analyzed. The exhausted column was regenerated with the help of 0.1 M HCl solution by up-flow method. The regenerated column was used for the next cycle of adsorption-desorption and the efficiency of the column was tested up to three cycles.

6.3 RESULTS AND DISCUSSION

The column experiments were performed at laboratory scale to examine the efficacy of GO/MgO for the removal of lead. Various column parameters such as initial lead concentration, bed height, and flow rate which were strongly influenced the column performance are discussed below. In addition to this various mathematical models i.e. Thomas, BDST, and Yoon–Nelson models were also applied to the experimental data for prediction and analyzing the breakthrough curves. In addition to it regeneration and reused studies of the exhausted column have also been carried out for the efficient utilization of the uptake capacity of the GO/MgO as a adsorbent.

6.3.1 Effect of bed height

Bed height is one of the important column parameter which has the significant effect on the column performance. The influence of bed height on the breakthrough curve was investigated at constant flow rate (1.66 mL/min) and initial lead concentration (80 mg/L) by altering the bed heights i.e. 2.5, 5, 7.5 cm. The resulting breakthrough curves corresponding to the bed heights are represented as Figure 6.1. The increase in bed height of the adsorption columns leads to an increase of breakthrough time along with the exhaustion time as well. It occurs because the amount of adsorbent increased in the column which leads to increase in service area [Auta and Hameed

(2014)]. It was also observed that treated volume of effluent also increased with the enhancement of bed height (Table 1). When the column with shorter bed height is used the axial dispersion become dominant over actual mass transfer process of the metal ions which retard the diffusion of the lead into the adsorbent [Taty-Costodes *et al.* (2005)]. The results shows that the uptake capacity also increased with increases in the bed height which can be attributed to the sufficient resident time of the lead in the adsorption column which provide the sufficient time for interaction of metal ions with the adsorbent. The treated volume increased from 4150 to 8300 mL as the bed height increases from 2.5 to 7.5 cm. In addition to it the larger bed height of the column also increase the availability of the more number of active adsorption sites for the metal ion. Table 6.1 shows that the treated volume of the effluent increased from 4150 mL to 8300 mL with the increase in bed height increases from 2.5 to 7.5 cm. Whereas, the uptake capacity was also enhanced from 172.5 mg/g to 187.9 mg/g as the bed height increased from 2.5 to 7.5.

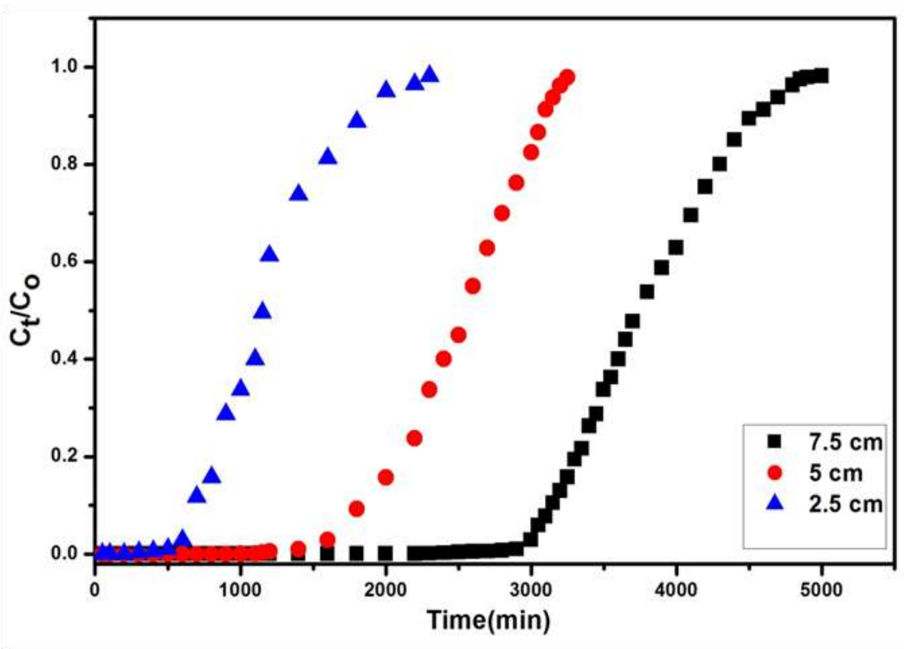

Figure 6.1. Breakthrough curve for lead adsorption at different bed heights

6.3.2. Effect of flow rate

The flow rate of the effluent is also a very important process parameters which strongly influenced the performance of the column. The effect of flow rate was studied at fixed bed height (7.5 cm), and initial lead concentration (80 mg/L) whereas the flow rate was adjusted to three flow rate i.e. 1.66, 3.32, and 4.98 mL/min. The breakthrough curves for lead adsorption corresponding to the different flow rate are shown in Figure 6.2. The parameter i.e. breakthrough time, exhaustion time, treated volume, and uptake capacity was calculated and are given in Table 6.1. It was observed that the breakthrough time exhaustion time, uptake capacity all are showing decreasing trend with the increase in flow rate from 1.66 to 4.98 mL/min. It was found that breakthrough time decreased from 2000 to 600 minutes and exhaustion time reduced from 5000 to 3650 minutes as the flow rates increased from 1.66 to 4.98 mL/min. When the column was operated at high flow rate due to inadequate utilization of adsorption bed is a common observable fact which causes the reduction in and residence time of the metal ion in the column [Hussain *et al.* (2011)].Therefore due to lesser residence time at the high flow rate, the metal ion did not interact strongly with the adsorbent and led to low adsorption capacity [Rahman and Khan (2016)]. Thus, the uptake capacity was decreased from 187.9 to 142.8 mg/g as the flow rate increases from 1.66 to 4.98 mL/min. Moreover, at the low flow rate, the adsorption process was dominated by external mass transfer which ultimately enhances the diffusion of the metal ion and leads to high uptake capacity (Vijayaraghavan *et al*. (2004)). Overall, from the above discussion, it can be concluded that for obtaining high adsorption capacity and to utilize the adsorbent efficiently the column must operate at low flow rate.

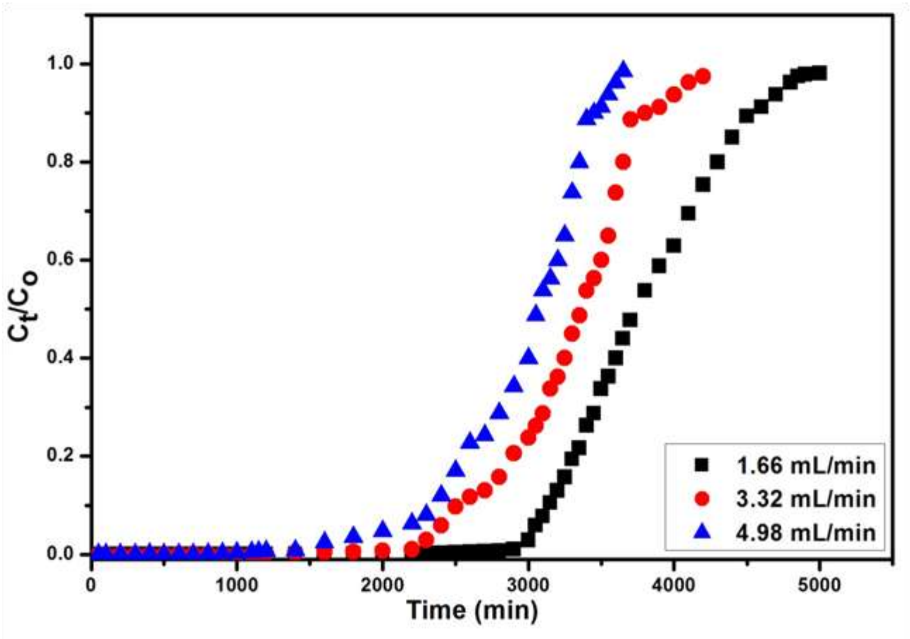

Figure 6.2. Breakthrough curve for lead adsorption at different flow rate

6.3.3 Effect of lead concentration

At a fixed bed height of 7.5 cm and a flow rate of 1.66 mL/min, the effect of 40, 60 and 80 mg/L inlet lead concentration on lead adsorption by GO/MgO was investigated. The breakthrough curves at different lead concentration are represented as Figure 6.3. The adsorption capacity was observed to be directly proportional to the influent concentration as it was increased with increase in influent concentration (Table 6.1).The increase in uptake capacity was attributed to the increase in concentration gradient which acts as the driving force for the metal adsorption. The adsorption capacity was increased from 95.3 to 187.9 when the lead inlet concentration was increased from 40 to 80 mg/L. It can be observed from the results (Table 6.1) that the treated volume of the effluent reduced from 10375 to 8300 mL with the increase in the concentration of lead ion from 40 to 80 mg/L. The extended breakthrough curves obtained at lower metal concentration was due to the lower mass transfer in the adsorption process hence; the large volume of lead contaminated water can be treated

[Unuabonah *et al*. (2010)]. It was also observed that as the initial concentration of the lead increased from 40-80 mg/L the breakthrough and exhaustion time both decreased. The breakthrough time decreased from 3350 to 2000 mL and exhaustion time falls from 6250-5000 mL as the inlet lead concentration increased from 40-80 mg/L. The reduction in breakthrough and exhaustion time at elevated metal concentration can be account by the fact that the adsorbent bed gets saturated quickly at high metal concentration which gives earlier exhaustion and breakthrough time.

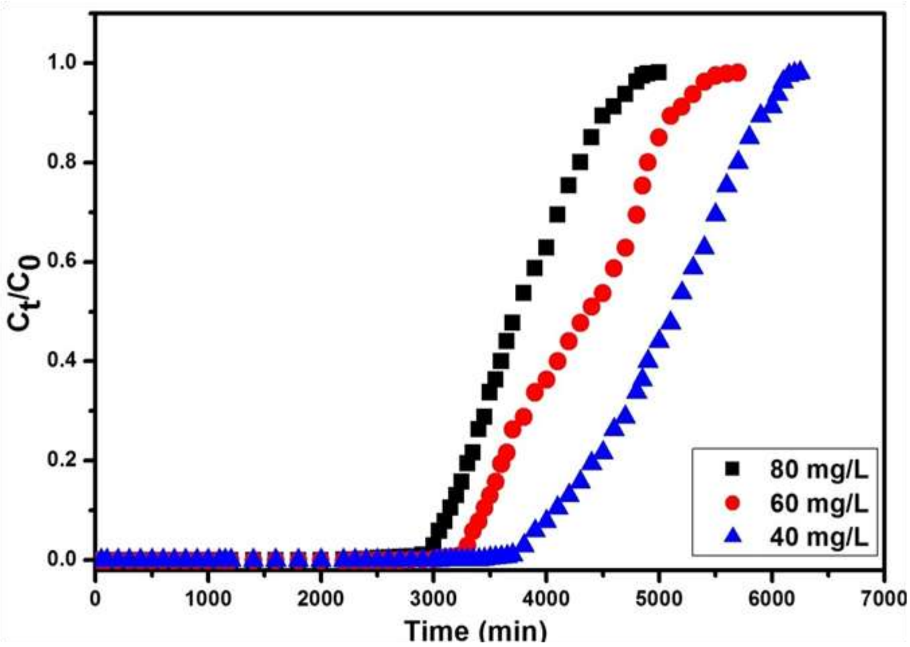

Figure 6.3 Breakthrough curve for lead adsorption at different lead concentration

Table 6.1 Adsorption data for fixed-bed GO/MgO column for lead adsorption at different process parameters.

Process parameters	Veff (mL)	t_b (min)	t_e (min)	q (mg/g)
Bed height Z (cm) (conditions : C_0= 80 mg/L, Q = 1.66 mL/min				
2.5	4150	400	2500	172.5
5	5395	1100	3250	179.2
7.5	8300	2000	5000	187.9
Flow rate Q (mL/min) (conditions : Co= 80 mg/L, Z = 7.5 cm				
1.66	8300	2000	5000	187.9
3.32	13944	1000	4200	166.5
4.98	18177	600	3650	142.8
Initial lead concentration (Z= 7.5 cm), Q = 1.66 mL/min)				
40	10375	3350	6250	95.3
60	9462	2700	5700	147.0
80	8300	2000	5000	187.9

6.3.4. Application of bed depth service time model (BDST)

The BDST model is the more up to date and widely used model which showed the relationship between service time and bed height. For this purpose, service time (exhaustion time) of the column corresponding to the bed heights of 2.5, 5, and 7.5 cm at flow rate of 1.66 and 3.32 mL/min at fixed lead concentration of 80 mg/L was determined. The BDST plots at different flow rates are given in Figure 6.4.

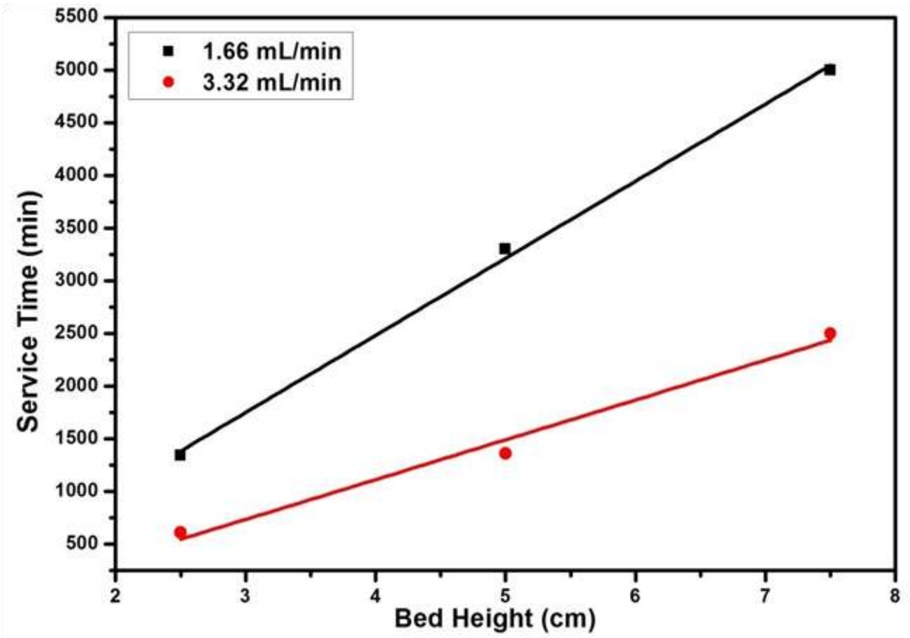

Figure 6.4 Bed depth service time plot for lead adsorption onto GO/MgO

The values of different parameters obtained by graph of service time and bed height and their corresponding correlation coefficient (R^2) are given in Table 6.2. The values of rate constant (k_a), adsorption capacity (N_0), and critical bed depth (Z_0) for both the flow rates was determined from the slopes and intercept of the respective graph and are summarized in Table 6.2. The high value of correlation coefficient i.e. 0.99 and 0.98 for the respective flow rate of the 1.66 and 3.32 mL/min showed that the variation of exhaustion time with the bed height was significantly linear thus advocated for the validity of BDST model. It was observed from the Table 6.2 the value of N_0 at the flow rates of 1.66 and 3.32 mL/min was found to be 158112 and 157680 mg/L. Thus the column capacity was decreased with the increase in flow rate. Table 6.2 also showed the values of rate constant (k_a) which was calculated from the respective slope of the BDST plot was observed to be 0.00025 and 0.00028 L/mg/min for the corresponding flow rate of 1.66 mL/min and 3.32 mL/min respectively. The rate constant of the BDST model can be defined as the rate of the transfer of pollutant species from liquid phase to solid phase. The rate constant values increased with the increase in flow rate of the effluent; thus it can be concluded that flow rate strongly affects the column performance. Accordingly, the inference can be drawn that the system kinetic in the initial phase of the adsorption followed external mass transfer process. The large value of k_a required shorted bed height while for the comparatively smaller value of k_a the longer bed is needed to avoid the breakthrough. Both the values i.e. column capacity and the rate constant values indicated that this adsorption system is highly efficient for lead removal by GO/MgO nanocomposite. Furthermore, the values of critical bed depth (Z_0) which was also evaluated from the BDST plots are also given in the Table 6.2. Its values found to be 0.58 and 1.31 cm for the respective flow rate of 1.66 mL/min and 3.32 mL/min respectively. The result revealed that value of Z_0 improved as the flow rate increases from 1.66 to 3.32 mL/min and this results was in agreement with the result of the breakthrough curve [Hasan and Srivastava (2009)].

Another benefit of the BDST model lies in the prediction and determination of the slope of unknown flow rate by using the slope of the known flow rate. As a result, it is possible to propose the operating conditions for the new fixed bed column for the unknown flow rate without experimentation. Thus, once the column parameters of a known flow rates are determined, then the fixed bed columns can be designed for other flow rates. Similar observation was also reported by Zulfadhly *et al*. (2001), Christian Taty-Costodes *et al*. (2005), Zou *et al.* (2013), Acheampong *et al*. (2013).

For the current adsorption system the BDST model was applied for the two flow rates i.e. 1.66 mL/min and 3.32 mL/min, and the results are displayed as Table 6.3. This modified equation of BDST was also applied to the data of new flow rate so that we can directly compare the experimental and calculated values. It was observed that the calculated and experimental values of slopes for the flow rate of 3.32 are similar. In addition, the intercept related to the slope remain unaltered as it was supposed to remain constant with the variation of flow rates.

Table 6.2 Bed depth service time (BDST) model parameters for the adsorption of lead

Flow rate	K_a (L/mg/min)	No (mg/L)	Z_o (cm)
1.66 mL/min	0.00025	158112	0.58
3.32 mL/min	0.00028	157680	1.31

Table 6.3 Experimental and predicted BDST model equations for the adsorption of lead.

Flow rate	Analysis	Fitted Equation	R^2
1.66 mL/min	Experimental	Y=732x-446.6	0.99
3.32 mL/min	Experimental	Y= 378x-400	0.98
3.32 mL/min	Predicted	Y=366x-446	0.99

6.3.5. Application of Thomas and Yoon–Nelson models

For the successful designing of the adsorption column, it is necessary to predict the breakthrough curve or concentration–time profile for the effluent**.** The Thomas model is one of the most general and widely used model to analyze the performance theory of the fixed bed column adsorption [Chen *et al*. (2012)]. Thomas model is based on two assumption that the adsorption process is not only governed by chemical interaction but along with it mass transfer at the interface also involved in the adsorption process and another assumption is that the experimental data follows the second-order kinetics and Langmuir isotherm model Foo et al. (2013)]. For the current adsorption system Thomas model was applied on the three different lead concentrations i.e. 40, 60, and 80 mg/L at the constant bed height (7.5 cm) and flow rate (1.66 mL/min) for the lead adsorption by GO/MgO nanocomposite. Thomas model can be represented by a linear plot of $\ln[(C_o/Ct) - 1]$ against time (t) at three different lead concentration which is shown in Figure 6.5. The values of various parameters i.e. k_{th} and q_{th} were determined from the intercept and slope of the respective plots which are summarized in Table 6.4 along with the R^2 values. The Regression coefficient (R^2) found to be 0.96, 0.96, and 0.99 for the corresponding lead concentration of 40, 60, and 80 mg/L. This result showed the good fit between the experimental and linearized forms of Thomas equation thus indicated toward the applicability of this model. Table 6.4 also indicated that the value of bed capacity (q_{th}) increased and the rate constant decreased with the increase in lead concentration. It is also clearly seen from the Table 6.4 that the bed capacity values calculated from experiments were in good agreement with the values of q_{th} which was predicted from the Thomas model. The above discussion revealed that the Thomas model can be used to describe the adsorption performance.

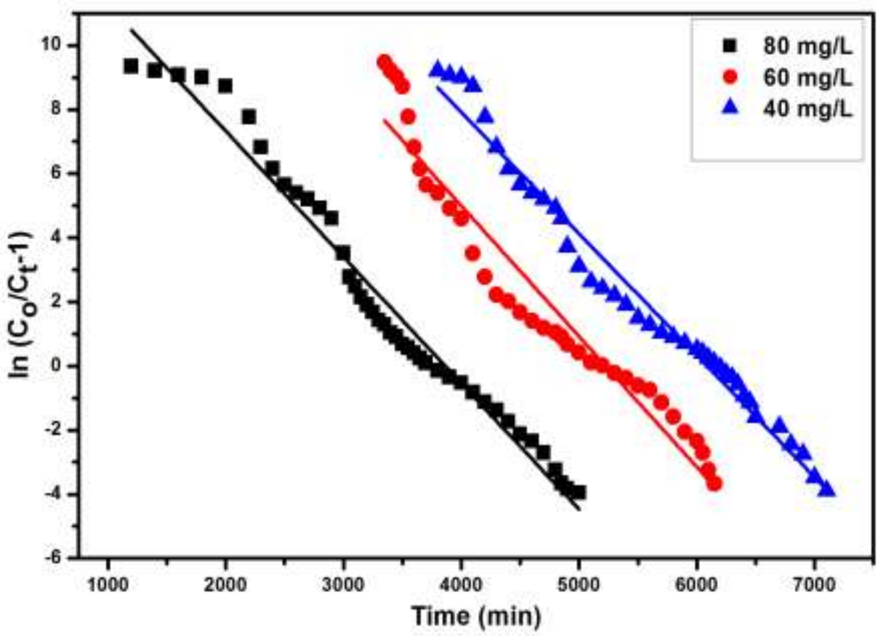

Figure 6.5. Adsorption curve according to Thomas model

The Yoon-Nelson model also applied to the experimental breakthrough data to predict the adsorption performance of fixed column study. The Yoon-Nelson model is less complicated than other models, and it also does not require detailed data about the adsorbate. The graph of Yoon-nelson model plotted in between ln [C_t/C_0-C_t] versus t (Figure 6.5) at lead concentrations of 40, 60, and 80 mg/L whereas, all the other parameters i.e. bed height and flow rate kept constant at 7.5 cm and 1.66 mL/min respectively. The values of k_{yn} ((rate constant (min^{-1})) and τ ((time required for 50% adsorbate breakthrough (min)) were calculated from slopes and intercept of the respective plots and are listed in Table 6.4 [H. El-Naas *et al*. (2017), Dotto *et al.* (2015), Yaghmaeian *et al*. (2014)]. Results showed that values of τ increased with the increase in metal concentration. Table 6.4 also contain the R^2 values 0.97, 0.96, 0.98 for the corresponding lead concentration of 40, 60, and 80 mg/L which advocated the validity of this model for the present adsorption system. It was found that time required for 50%

breakthrough concentration decreased with the increase in initial inlet lead concentration.

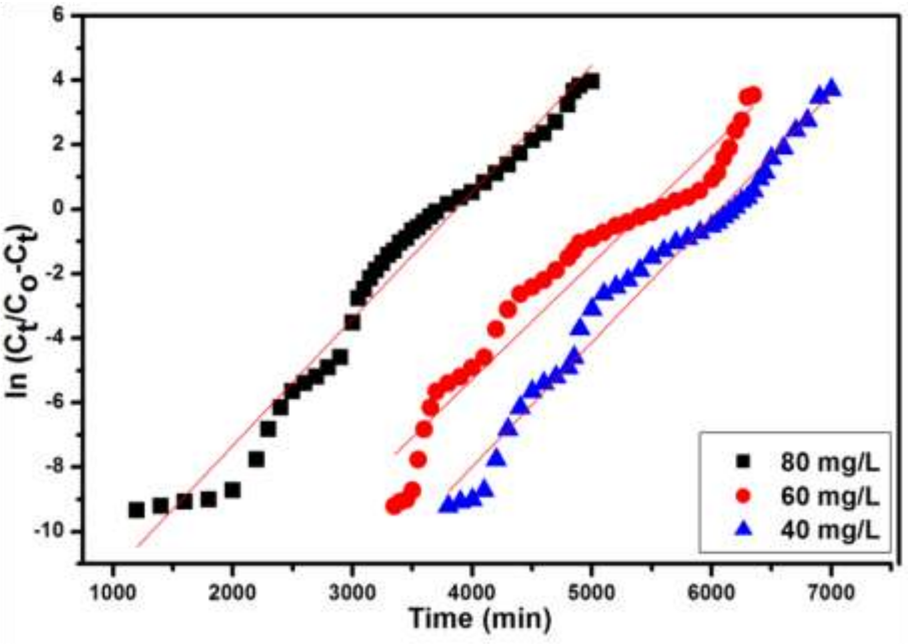

Figure 6.6. Adsorption curve according to Yoon-Nelson model

This fact can be account as the column exhaust more rapidly as the metal concentration increases which cause the reduction in the τ value. Therefore we can conclude that both the models i.e. Thomas and Yoon–Nelson models were both successfully utilized for the prediction of the breakthrough curves for this adsorption system.

Table 6.4 Parameters predicted from the Thomas and Yoon–Nelson models for the adsorption at different lead concentrations.

	Thomas Model			Yoon Nelson Model			
Lead conc. (mg/L)	**K_{TH} (min^{-1})**	**q_{TH} (mg/g)**	**R^2**	**K_{YN} (L/min)**	**$\tau_{(exp)}$ (min)**	**$\tau_{(cal)}$ (min)**	**R**
40	0.00005	17.2	0.96	0.004	5200	5263	0.97
60	0.00004	42.7	0.96	0.0036	4400	4472	0.96
80	0.000008	45.6	0.99	0.0035	3700	3718	0.98

6.3.6 Regeneration

Desorption of loaded metal ion and the subsequent regeneration of the adsorbent is of vital importance for the economic development. Thus, the desorption and regeneration studies are essential in order to ensure the long-term repeated use of the adsorbent and to reduce the treatment cost. Multiple utilization of the adsorbent is necessary for the large-scale adsorption system which is requisite for the industrial application. It is also important to mention here that regeneration must produce the small volume of metal concentrate devoid of damaging the adsorbent as it will affect the uptake performance of the adsorbent. For this adsorption system, 0.1 M HCl used as a regenerating reagent for desorption of lead from the GO/MgO. For this purpose, the fixed bed column was eluted with the 0.1 M HCl to regenerate the adsorbent bed and investigate its adsorptions performance up to the three sorption–desorption cycle. The regeneration experiments were performed with the column packed with sufficient GO/MgO nanoadsorbent in order to achieve the bed height of 7.5 cm, at the constant flow rate (1.66 mL/min) and initial lead concentration (80 mg/L). Figure. 6.7 shows the breakthrough curves for three adsorption-desorption cycles. The regeneration efficiency was found to be greater than 97% with 0.1 M HCl for all the three cycles. The breakthrough time was decrease with the successive cycle of adsorption-desorption from 5000 to 4500 min from the cycle I to III. However, high uptake capacity was obtained in all the three cycle with a slight reduction in its values. Table 6.5 showed that the elution time reduced from 240 to 185 with the progress of adsorption-desorption cycle from I to III. The elution efficiency greater than 97% for the lead adsorption by GO/MgO nanocomposite also advocated for the contribution of ion exchange mechanism in the adsorption of lead (Baral et al. (2009)). The findings also suggested that the prepared nanocomposite of GO/MgO was a potential adsorbent for the lead removal by fixed bed up flow column method.

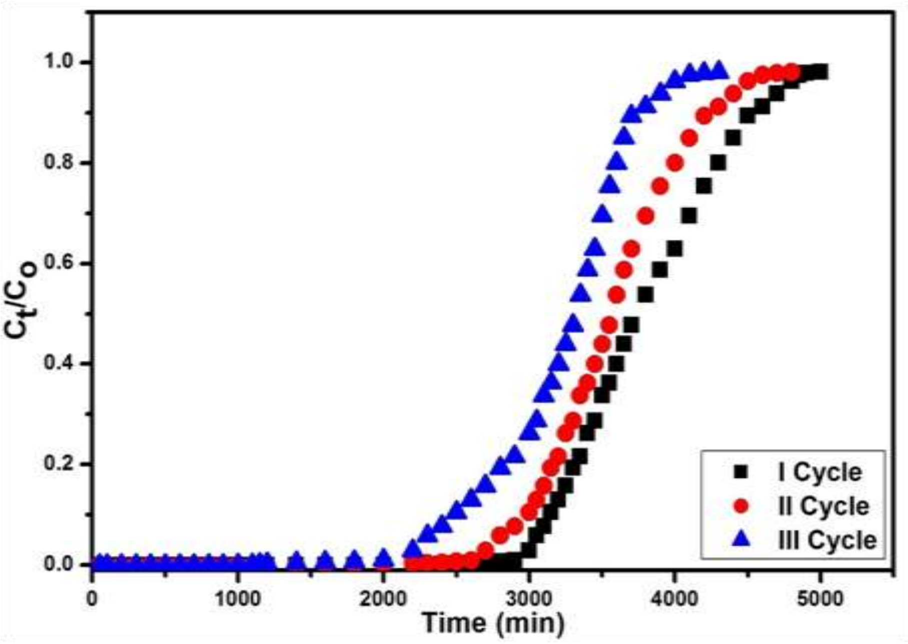

Figure 6.7. Breakthrough curves for lead adsorption onto GO/MgO during three adsorption-desorption cycles

Table 6.5 Adsorption process parameters for three sorption–desorption cycles of lead onto GO/MgO nanocomposite

Cycle	V_{eff}(mL)	t_b(min)	t_e(min)	q (mg/g)	Elution Time (min)	Elution Efficiency (%)
I	8300	2000	5000	187.9	240	89.35
II	7968	1400	4800	176.8	205	93.23
III	7470	1100	4500	166.0	185	97.07

6.3.7 Adsorption column life factor

The regeneration study showed that the breakthrough time reduced with the progress of regeneration cycles which resulted in the broadening of mass transfer zone [Vijayaraghavan *et al.* (2005)]. This trend was observed mainly due to gradual deterioration of the adsorbent because of continuous usage. Thus the decrease in adsorption performance of the column with the progress of elution cycle can be predicted on the basis of some important column parameters. In the present adsorption system, the activity-indicator was calculated as ''life-factors'' based on the bed uptake capacity and breakthrough time [Volesky *et al*. (2003)]

The life factor of the column can be determined by using a linear regression equation given by Volesky [Volesky *et al*. (2003)]:

$$t_b = t_{bi} + K_L n$$

(6.1)

where t_{bi} is the initial breakthrough time (min), n represents the number of adsorption desorption cycle and K_L is the corresponding life factor (min/cycle). The values of t_{bi} along with its corresponding life factor K_L were determined from the graph of t_b versus n and the relationships t_b=2350-350n was predicted. From this relationship it was found that the column bed would be capable to avoid the breakthrough time at t = 0 up to 6.7 cycle for lead removal.

Similarly, in order to calculate the life factor in terms of breakthrough time, the following regression was used:

$$q = q_i + K_L n$$

(6.2)

Where qi stand for the initial uptake capacity (mg/g) and K_L is the corresponding life factor (per cycle). The value of qi and K_L was determined by the equation q=11.5n-199.6. It was predicted from the equation that the column bed would be completely exhausted after 17.3 cycles. Thus, the life factors calculation in terms of breakthrough time and column uptake capacity utilized to evaluate the adsorption performance of column. Figure 6.8 Linear plot of breakthrough time and lead uptake and critical bed length with respect to the number of cycles

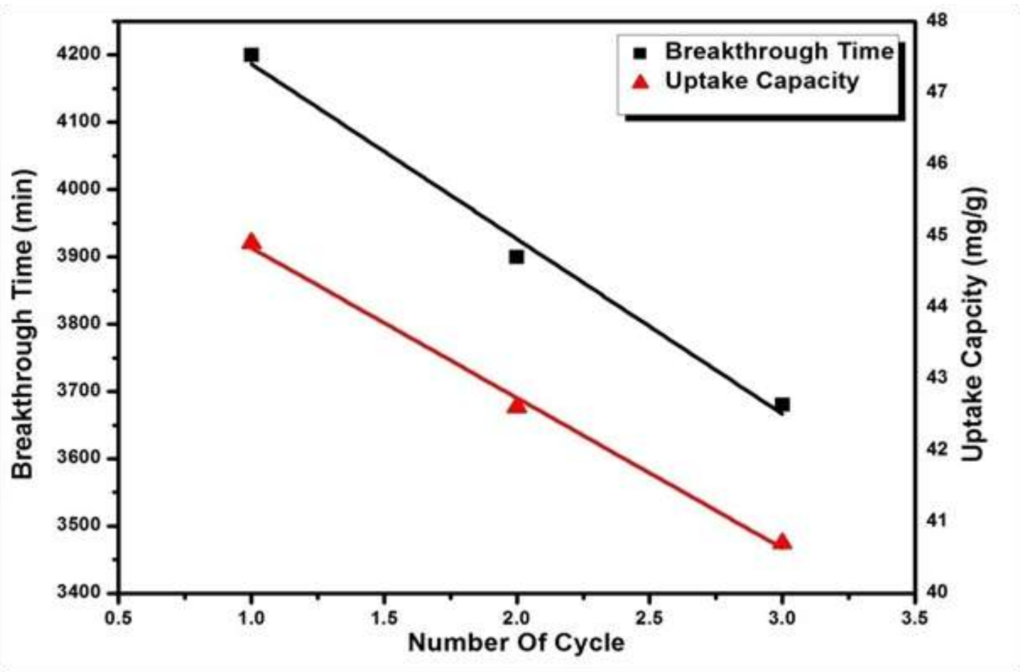

Fig. 6.8. Linear plot of breakthrough time and lead uptake and critical bed length with respect to the number of cycles

6.4 CONCLUSION

This chapter deals with the removal of toxic lead from aqueous solution by continuous fixed bed column system from the aqueous solution in terms of breakthrough curves. The adsorption performance of lead was strongly affected by variation in inlet Lead concentration, flow rates as well as bed height. The adsorption performance of the column improved with increase in bed height whereas, decreased with increase in flow rate. However, the column uptake increased with increase in inlet Lead concentration. The maximum uptake was found to be 187.9 mg/g at flow rate of 1.66 mL/min and 7.5 cm of bed height. The BDST model was successfully applied in order to predict the relation between service time and bed height which was important to design the column. The BDST model was also utilized for prediction of column parameters to design new column for the flow rate of 4.98 mL/min from a sample flow rate of 1.66 mL/min. The experimental kinetic data successfully applied to the mathematical models i.e. Thomas and Yoon-Nelson models which were well fitted to these models and the studies were useful for application of the large scale field application. The column was regenerated with the 0.1M HCl solution and the adsorption performance was evaluated up to the three adsorption-desorption cycle. The elution efficiencies was observed to be greater than 97% for Lead indicated the presence of ion exchange in the removal process. The column adsorption life factor predicted the life of the adsorbent and for this case the adsorbent was anticipated to have enough capacity to avoid the breakthrough at time t=0 for up to 6.7 cycles and it was also predicted that the bed would be completely exhausted (zero uptake) after 17.3 cycles.