Research Article

Removal of Pb^{2+} Ions by ZSM-5/AC Composite in a Fixed-Bed Bench Scale System

R. Lakshmipathy, G. L. Balaji, and Iván Leandro Rodríguez Rico

1Department of Chemistry, KCG College of Technology, Karapakkam, 600097, Chennai, Tamilnadu, India
2School of Advanced Sciences and Languages, VIT Bhopal University, 466114, Bhopal, Madya Pradesh, India
3Faculty of Chemical and Pharmacy, Department of Chemical Engineering, Central University "Marta Abreu" of Las Villas, Cuba

Correspondence should be addressed to R. Lakshmipathy; lakshmipathy.che@kcgcollege.com and Iván Leandro Rodríguez Rico; ivanl@uclv.edu.cu

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This investigation suggests the implementation of ZSM-5 activated carbon composite as a prolific adsorbent for the continuous elimination of Pb^{2+} ions from water. Continuous adsorption experiments were performed by varying three parameters such as process flow rate (2-6 mL min^{-1}), bed height (2-6 cm), and initial concentration (250–750 mg L^{-1}). The highest loading capacity of the fixed-bed 750 mg L^{-1} was achieved with optimal values of 2 mL min^{-1} of flow rate, bed height of 6 cm, and initial concentration of 750 mg L^{-1}, respectively. The breakthrough curves and saturation points were found to appear quickly for increasing flow rates and initial concentration and vice versa for bed depth. The lower flow rates with higher bed depths have exhibited optimal performances of the fixed-bed column. The mechanism of adsorption of Pb^{2+} ions was found to be ion exchange with Na^{+} ions from ZMS-5 and pore adsorption onto activated carbon. The breakthrough curves were verified with three well-known mathematical models such as the Adams-Bohart, Thomas, and Yoon-Nelson models. The later models showed the best fit to the column data over the Adams-Bohart model that can be utilized to understand the binding of Pb^{2+} ions onto the composite. Regeneration of ZSM-5/activated carbon was achieved successfully with 0.1 M HCl within 60 min of contact time. The outcomes conclude that ZSM-5 activated carbon composite is a prolific material for the continuous removal of water loaded with Pb^{2+} ions.

1. Introduction

The burgeoning population and swift industrialization have led to the intense release of contaminant-loaded effluents into the natural ecosystem. Industries such as batteries, pigments, and glass widely use lead (Pb), and the effluents contain a considerable amount of Pb^{2+} ions. Lead is a heavy metal that is nonbiodegradable and carcinogenic to human and aquatic life [1]. Therefore, it is highly essential to remove the Pb^{2+} ions from industrial effluents to conserve the natural ecosystem.

Various physical and chemical treatment techniques such as ion exchange [2], membrane filtration [3], flocculation [4], coagulation [5], adsorption [6], solvent extraction [7], chemical precipitation [8], and electrochemical treatments [9] are developed for the remediation of wastewater laden with heavy metal ions. Ion exchangers were quite popular for the removal of heavy metal ions from wastewater, and resins are usually employed as prolific ion exchangers [2]. Membranes are another important class of technique that is efficient in the removal of heavy metal ions from wastewater [3]. However, the cost of the ion exchangers and membranes limits the applications [10]. Similarly, flocculation and coagulation have disadvantages such as disposal and use of toxic chemicals [11]. The chemical extractions are quite useful, but the cost of the solvents, disposal of precipitations, and energy requirements limit the applications [12].
Adsorption is one of the powerful and well-established techniques for wastewater treatment due to its simplicity and economic factors [13]. In recent decades, adsorbents from agricultural sources have been developed, and these adsorbents are economical and do not cause any disposal issues unlike chemical precipitations or coagulation and flocculation [14]. Adsorption does not require any energy requirements such as electrochemical treatments [15]. Furthermore, the aptness of adsorption to eliminate hazardous contaminants without generating any toxic byproducts and retaining the standards of water unaltered has also favored it [16]. Adsorbents such as activated carbon [17], zeolites [18], nanosorbents [19], and biopolymers [20] were found to be effective and efficient sorbents for the remediation of contaminated water. In an interesting study, Hanbali et al. [21] reported the use of magnetic multiwalled carbon nanotubes as potential adsorbents for the removal of Pb\(^{2+}\) ions. The loading capacity was found to be 9.09 mg g\(^{-1}\) at a pH of 8. Mohd et al. [22] reported the modified palm oil industry solid waste as a useful adsorbent for the removal of Pb\(^{2+}\) ions. The maximum removal efficiency of fruit bunch of palm was reported to be 92.2 mg g\(^{-1}\) at a pH of 1 with a contact time of 15 min. Iron oxide nanocomposites produced from biowaste were reported for the removal of Pb\(^{2+}\) ions [23]. The T-Fe\(_2\)O\(_4\) exhibited 95% removal efficiency with a contact time of 95 min at pH 4.5.

Zeolites are naturally available crystalline microporous solids that form a network of cavities and channels [24]. They are proven to be very good adsorbents, ion exchangers, and catalysts [25]. Alumino-silicate zeolites (ZSM-5) are microporous materials that are commonly used in the isomerization of hydrocarbons in the petro industry as catalysts [26]. Natural zeolites are prolifically utilized as adsorbents for the sequestration of Pb\(^{2+}\) ions [27]. The NaX zeolite exhibited an adsorption capacity of 14.2 mg g\(^{-1}\) at pH 6 with a contact time of 60 min. ZSM-5 zeolites are modified with several organic and inorganic compounds and elements to enhance the sorption capacity. Polyvinyl alcohol and carboxymethyl cellulose-incorporated zeolites are utilized for the effective adsorption of synthetic organic molecules from aqueous solution [28]. ZSM-5 modified with mixed metal oxides was found to be potential adsorbents for the removal of elemental mercury [29]. However, the literature reveals that very little study is available on the application of the natural and modified ZSM-5 zeolites for the sequestration of cations. The majority of studies report the elimination of cationic contaminants from aqueous solution by batch and fixed-bed method. The potential of ZSM-5 zeolites for the elimination of cations in the batch process is investigated but in continuous columns is yet to be explored. The synthesis of ZSM-5 activated carbon composite and its potential use for the remediation of Pb\(^{2+}\) and Cd\(^{2+}\) ions from contaminated water have been reported [30].

In continuation of the above, the present investigation describes the sequestration of Pb\(^{2+}\) ions through the fixed-bed process by using ZSM-5 activated carbon composite as an ecofriendly sorbent. The impacts of various governing components were investigated, and various breakthrough models were adopted to analyze the experimental data.

2. Materials and Methods

2.1. Reagents. Tetraethyl orthosilicate and Sodium Aluminate were obtained from Sd fine chemicals. Tetra propyl ammonium hydroxide and lead nitrate were obtained from Merck chemicals. Distilled water was used for all the experiments. Hydrochloric acid, acetic acid, and Sodium Hydroxide were obtained from Sd fine chemicals. Activated carbon was obtained from local chemical suppliers, and all the reagents used were of AR grade.

2.2. Preparation of ZSM-5/Activated Carbon Composite and Metal Stock Solution. The ZSM-5 activated carbon composite was prepared by mixing 10 mL of tetraethyl orthosilicate (TEOS), 3 g of Sodium Aluminate (NaAlO\(_2\)), and 2 g activated carbon (AC). The mixture was stirred overnight followed by drying at 80°C for 12 h. After drying, a gel was obtained which was added to 15 mL of tetra propyl ammonium hydroxide, mixed by stirring, and dried overnight at 100°C. The dried gel was kept in a vial which was then placed in an autoclave containing 2 mL of water. Then, it was heated in an oven at 170°C for 72 h. The added water that generated steam assisted in the dry gel conversion. The resulting dried sample was calcined in a tubular furnace at 550°C for 3 h under N\(_2\) flow (150 mL/min). The dried and calcined sample was named ZSM-5/AC which was found to be around 0.5 μm in size and used for further investigation. Lead (II) nitrate (1.6 g) was solubilized in one litre of demineralized water to prepare 1000 mg L\(^{-1}\) of metal ion stock solution, and 0.01 M hydrochloric acid (HCl) and Sodium Hydroxide (NaOH) were used for the pH adjustments.

2.3. Fixed-Bed Column Investigations. A small-scale glass column with a height of 15 cm having an internal diameter of 10 mm was chosen for performing the fixed-bed column investigations (Figure 1). Firstly, the glass column was filled with ZSM-5/AC (1.112 g cm\(^{-1}\)), and the Pb\(^{2+}\) ions were pumped into the top of the column with the help of a peristaltic pump with a desired rate of flow. The eluents were saved at various preset time intervals at the exit of the fixed-bed. An atomic absorption spectrophotometer (AA240, Varian) was utilized to estimate the residual concentrations of collected samples. To investigate the influence of rate of flow for the elimination of Pb\(^{2+}\) ions by ZSM-5/AC, investigations were performed with varying flow rates from 2 to 6 mL min\(^{-1}\) with a difference of 2 mL. The influence of bed depth was investigated by deferring the bed depth from 2 to 6 cm in height with a height interval of 2 cm, and the remaining influential parameters were kept constant. Further to the optimization of bed height and flow rate, the influence of adsorbate concentration was experimented with by deferring the initial concentration of Pb\(^{2+}\) ions from 250 to 750 mg L\(^{-1}\). The inlet of Pb\(^{2+}\) ions was continued until the inlet and exit concentration was found to be unchanged suggesting the saturation of the column [31]. To ensure that the data analysis was accurate and reproducible, the fixed-bed investigations were performed thrice and the mean values were considered with a standard deviation of less than 4%.
2.4. Fixed-Bed Data Analysis. The breakthrough curves are the output of experimental runs from packed bed column studies. In general, the behaviour and dynamic reply of adsorption in columns can be easily determined from the time and figure of the breakthrough curve that is considered to be an imperative characteristic [32]. The breakthrough position of the S form curve is examined when the eluent concentration \( (C_e) \) from the fixed-bed attains about 0.1% of influent concentration. The exhaustion of fixed-bed is attained when the position of concentration of eluent attains 95% or above. The volume of effluent \( (V_{eff}) \) can be understood with equation

\[
V_{eff} = Q t_{total},
\]

where \( Q \) is the volumetric rate of flow and \( t_{total} \) is the complete flow time (min).

The amount of \( \text{Pb}^{2+} \) taken up, \( M_{ad} \) (mg), in the sorption bed can be determined by the following equation:

\[
M_{ad} = \frac{Q}{1000} \int_{t=0}^{t=total} C_{ad} dt,
\]

where \( C_{ad} \) is the amount of \( \text{Pb}^{2+} \) ions removed (mg L\(^{-1}\)).

The absolute quantity of \( \text{Pb}^{2+} \) ions getting into the bed \( (M_{total}) \) can be estimated from equation

\[
M_{total} = \frac{C_0 Q t_{total}}{1000},
\]

where \( C_0 \) is the initial concentration of the \( \text{Pb}^{2+} \) ions.

Finally, the total \( \text{Pb}^{2+} \) ion removal percentage is known from equation

\[
Y \ (%) = \frac{M_{ad}}{M_{total}} \times 100,
\]

where \( Y \) is the yield percentage.

2.5. Column Breakthrough Curve Modeling. The simple mathematical models can well explain the prolific behaviour of lab-scale column processes to large-scale processes typically used in industries [33, 34]. The familiar and common mathematical models such as Adams-Bohart, Thomas, and Yoon-Nelson models were employed in understanding the breakthrough curves obtained for various influential parameters of the column.

One of the commonly considered models in the understanding of breakthrough curves is the Adams-Bohart model [35]. This model suggests that the fraction of loading magnitude is proportional to the rate of sorption and further suggests that the equilibrium is not instantaneous [36, 37]. The major advantage is that the initial part of the breakthrough curve is very well inferred, and the equation is conveyed as below:

\[
\ln \frac{C_t}{C_0} = k_{AB} t - k_{AB} N_z \frac{z}{U_o},
\]

where \( C_0 \) and \( C_t \) are the entry and exit concentrations of \( \text{Pb}^{2+} \) ions (mg L\(^{-1}\)), \( k_{AB} \) is the kinetic constant (L mg\(^{-1}\) min\(^{-1}\)), \( N_z \) is the exhaustion amount (mg L\(^{-1}\)), \( z \) is the depth of the bed (cm), and \( U_o \) is the peripheral velocity (cm min\(^{-1}\)).

The Thomas model is the best-known theoretical model for explaining the efficiency of binding of lead ions onto an adsorbent in a packed bed column [38]. The plug flow process in a packed column is the assumption made by the Thomas model, and the model equation is given as below:

\[
\ln \left( \frac{C_t}{C_0} - 1 \right) = k_{Th} q_m \frac{m}{Q} - k_{Th} C_0 t,
\]

where \( k_{Th} \) is considered constant of the Thomas model (mL min\(^{-1}\) g\(^{-1}\)), \( m \) is the mass of the adsorbent, and \( q_m \) is the loading magnitude (mg g\(^{-1}\)).

One of the simplest methods and models for the adsorption of gas-phase molecules onto activated coal was proposed by Yoon and Nelson [39]. Yoon and Nelson considered that the decrease in the rate in the likelihood of sorption of \( \text{Pb}^{2+} \) is comparable to the likelihood of sorbate sorption and the prospect of \( \text{Pb}^{2+} \) ion breakthrough on ZSM-5/AC. The linearized equation of this model is expressed as

\[
\ln \left( \frac{C_t}{C_0 - C_t} \right) = k_{YN} t - \tau k_{YN},
\]

where \( k_{YN} \) is the proportionality constant in min\(^{-1}\) of the Yoon-Nelson model and \( \tau \) is the 50% retaining time of the initial sorbate (min).

3. Results and Discussion

3.1. Influence of Rate of Flow. One of the crucial parameters in the removal of contaminants from wastewater especially during the continuous treatment process is flow rate. Therefore, in the present investigation, the rate of flow was varied between 2 and 6 mL min\(^{-1}\) at fixed column length (2 cm) and opening concentration (250 mg L\(^{-1}\)) for the sequestration of...
Pb\textsuperscript{2+} ions by ZSM-5/AC from aqueous solution. The breakthrough curves obtained for different rates of flow are represented in Figure 2. It is observed that with the burgeoning flow rate, the breakthrough and saturation time tend to decrease. This is well elucidated on the reality that, at a minimal rate of flow, the time of residence of Pb\textsuperscript{2+} ions to interact with the surface of the ZSM-5/AC is high. At higher flow rates, the time for adsorption onto the surface or pore diffusion decreases. It is also seen that the breakthrough curves became steep with an increase in flow rates suggesting the faster saturation of column and lesser time spent by the metal ion. Hence, the efficiency and breakthrough time decrease with burgeoning flow rates. Similar observations have been reported for the continuous sorption of Pb\textsuperscript{2+} ions in the column by WR powder [16].

| \( C_0 \) (mg L\(^{-1}\)) | \( Q \) (mL min\(^{-1}\)) | \( Z \) (cm) | \( M_{ad} \) (mg) | \( M_{total} \) (mg) | \( Y \) (%) | EBCT (min) |
|---------------------|-----------------|--------|---------------|-----------------|-------|----------|
| 250                 | 2               | 2      | 136.6         | 200             | 68.6  | 2.3      |
| 250                 | 4               | 2      | 190.6         | 300             | 63.5  | 1.7      |
| 250                 | 6               | 2      | 186.6         | 330             | 56.5  | 1.2      |
| 250                 | 2               | 2      | 136.6         | 200             | 68.6  | 2.3      |
| 250                 | 2               | 4      | 161.0         | 225             | 71.5  | 4.5      |
| 250                 | 2               | 6      | 213.3         | 270             | 79.0  | 6.5      |
| 500                 | 2               | 6      | 154.7         | 225             | 68.7  | 6.5      |
| 750                 | 2               | 6      | 93.5          | 175             | 53.2  | 6.5      |

3.2. Influence of Height of Bed. The influence of the height of the bed for the removal of Pb\textsuperscript{2+} ions by ZSM-5/AC was explored by changing the bed height between 2 and 6 cm, and the breakthrough shapes attained are represented in Figure 3. With the burgeoning bed heights, the time of saturation and breakthrough extends, and further, removal efficiency also increased with increasing bed heights. The time of breakthrough extends from 150 to 400 min with augmenting the height of the bed from 2 to 6 cm. The empty bed column time (EBCT) also extended from 2.3 to 6.5 min (Table 1). This is attributed to the fact that the Pb\textsuperscript{2+} ions have more chance to interact with the ZSM-5/AC and more surface active sites are available for interaction. Hence, the removal efficiency and adsorption capacity increase at higher bed heights. Similar observations have been reported for the removal of Pb\textsuperscript{2+} ions by dead calcareous skeletons [40].

3.3. Influence of Initial Concentration. The influence of Pb\textsuperscript{2+} ions on the breakthrough shapes was experimented by considering the concentrations from 250 to 750 mg L\(^{-1}\) and the respective breakthrough; shapes are illustrated in Figure 4. As observed from the figure, various crucial components decreased with burgeoning Pb\textsuperscript{2+} ion concentrations such as removal efficiency, breakthrough, and exhaustion time. The total amount of influent passing into the fixed-bed also reduced with burgeoning entry concentration (Table 1). The observations suggest that the time taken for the attainment of 50% breakthrough tendency reduced with burgeoning initial metal ion concentration. This can be expounded on the basis that a minimal concentration gradient resulted in moderate adsorption of Pb\textsuperscript{2+} ions due to the reduced diffusion coefficient and reduced mass transfer coefficients [20]. Hence, lower concentrations will benefit the increased diffusion coefficient and increased mass transfer coefficients resulting in greater adsorption efficiency. Similar observations have been reported for the removal of Pb\textsuperscript{2+} ions by natural clinoptilolite [41].

3.4. Modeling of Breakthrough Curves. The design of fixed-bed columns and its prediction can be carried out from breakthrough curves of studied parameters. The scale-up of lab-scale process to industrial process can be performed by various mathematical models that have been put forward.
In the present investigations, the vital actions of the fixed-bed column were studied and analyzed with the Adams-Bohart, Thomas, and Yoon-Nelson models.

3.4.1. Adams-Bohart Model. For parameter assessment, the range of \( t \) values was considered from 0 to 0.5 \( C_0/C_t \) of the breakthrough shapes. The slope \( K_{AB} \) and intercept \( N_o \) were tabulated from the graph of \( \ln(C_0/C_t) \) vs. \( t \) (figure not shown), and the respective values and correlation coefficients are outlined in Table 2. As outlined in Table 2, the \( K_{AB} \) values increased with growing bed depth and tend to drop with the growing rate of flow and preliminary \( \text{Pb}^{2+} \) ion concentration. The results suggested that the external mass transfer dominated the overall kinetics of the process [42]. The applicability of the Adams-Bohart model for understanding the beginning of breakthrough curves of the present process was elucidated by the moderately high correlation coefficients.

3.4.2. Thomas Model. The performance prediction of the breakthrough of columns can be very well described by the Thomas model. The constants and respective coefficients of correlation derived for the Thomas model from the linear regression equation are summarized in Table 3. The values of \( K_{TB} \) are observed to reduce with an increase in bed height, but the opposite trend was observed with a burgeoning rate of flow and preliminary concentration. But \( q_o \) depicted the opposite trend to that of \( K_{TB} \). The correlation coefficients obtained are found to be very high suggesting the suitability of the model for the removal of \( \text{Pb}^{2+} \) ions by ZSM-5/AC. These observations suggest that the Thomas model was applicable for the adsorption of \( \text{Pb}^{2+} \) ions and the rate-limiting step was not just due to internal and external mass transfer [31].

3.4.3. Yoon-Nelson Model. The correlation coefficients and values of \( K_{YN} \) and \( \tau \) acquired using the linear regression analysis for breakthrough curves are outlined in Table 4. The coefficients of correlation were between 0.955 and 0.993, suggesting the applicability of the Yoon-Nelson model in addition to the Thomas model. The \( K_{YN} \) values were found to decrease with a surge in preliminary concentration but increase with the growing rate of flow and bed depth. The component \( \tau \) which is considered a time for 50% retention was observed to surge with surging bed height due to relaxed exhaustion of the column at elevated peaks of packed beds. On the other end, the \( \tau \) values profoundly reduce with the burgeoning flow rate and preliminary entry concentration [26]. This is due to the quick attainment of exhaustion of fixed-bed columns [41]. This observation suggests that both Yoon-Nelson and Thomas models describe well for the elimination of \( \text{Pb}^{2+} \) ions by ZSM-5/AC from an aqueous solution.

3.5. Regeneration of ZSM-5/AC. Desorption of \( \text{Pb}^{2+} \) ions and revival of ZSM-5/AC studies were carried out to investigate the reusability capacity of ZSM-5/AC. Desorption studies were performed with two desorbing agents such as 0.1 M CH₃COOH and 0.1 M HCl. Initially, the fixed-bed column...
was packed with Pb\textsuperscript{2+} ion-loaded ZSM-5/AC for 6 cm, and the desorbing agent was allowed to flow from the top of the column with a flow rate of 2 mL/min. The pH of the desorbing agents was pH 1.2 and 3.0, respectively, for 0.1 M HCl and 0.1 M CH\textsubscript{3}COOH. The eluent was collected at the exit of the column at fixed time intervals, and the amount of Pb\textsuperscript{2+} ions desorbed was calculated using an atomic absorption spectrometer. Desorption of Pb\textsuperscript{2+} ions versus time plot is represented in Figure 5. It can be observed that initially the amount of Pb\textsuperscript{2+} ions in the eluent was found to be high and gradually decreased with an increase in time. The high amount of Pb\textsuperscript{2+} ion concentration released at the initial time period is due to ion exchange with the H\textsuperscript{+} ions of desorbing agents. The decrease in concentration with respect to time is due to exhaustion of Pb\textsuperscript{2+} ions and regeneration of ZSM-5/AC. The maximum desorption efficiency of ZSM-5/AC was found to be 83% and 92%, respectively, for 0.1 M CH\textsubscript{3}COOH and 0.1 M HCl solutions. The higher efficiency observed for HCl over CH\textsubscript{3}COOH was due to the strength of the acids. Stronger acids exhibit higher desorption efficiency due to the quick release of H\textsuperscript{+} ions compared to weak acids such as CH\textsubscript{3}COOH. The high revival efficiency exhibited by ZSM-5/AC was due to the exchange of Pb\textsuperscript{2+} ions with hydronium ions. The ion exchange capability of zeolites helped in the effective regeneration of the composite materials. These results suggest that ZSM-5/AC could be efficiently considered in repeated cycles for the elimination of Pb\textsuperscript{2+} ions from an aqueous solution.

3.6. Adsorption Potential. The supreme adsorption potential of ZSM-5/AC towards Pb\textsuperscript{2+} ions was calculated to be 213.3 mg g\textsuperscript{-1} which was considered to be very significant in comparison to many other reported adsorbents in the literature (Table 5). The higher loading potential was due to the combined effect exhibited by porous ZSM-5 and activated carbon materials. The adsorption of Pb\textsuperscript{2+} ions onto ZSM-5/AC could be due to pore adsorption as well as binding onto acidic sites present on the surface of the activated carbon.

4. Conclusion

This study utilized the ZSM-5/AC composite as an adsorbent for the removal of Pb\textsuperscript{2+} ions from an aqueous solution and explored its potential in a fixed-bed column. It was observed that low flow rate, higher bed height, and lower initial inlet concentration yielded maximum removal efficiency for Pb\textsuperscript{2+} ion removal by ZSM-5/AC. The breakthrough curves were predicted with linear regression models such as the Adams-Bohart, Thomas, and Yoon-Nelson models. Based on the coefficients of correlation and relative constants, all three models were found to fit and well describe the breakthrough curves. Desorption and regeneration studies suggested that ZSM-5/AC could be repeatedly used for several cycles. These results conclude that ZSM-5/AC is a prolific composite material for the sequestration of Pb\textsuperscript{2+} ions from water streams.

Data Availability

All the required data are available in the manuscript itself.

Conflicts of Interest

The authors declare that they have no conflicts of interest.
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