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Modeling and gPROMS based simulation of adsorption process for the removal of Cu (II) from aqueous wastewater

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The present work studies the performance of Indion 730 (Strong acid) ion exchange resin for the removal of Cu (II). The modeling and gPROMS based simulation is used to study the sorption capacity, equilibrium, and performances of Indion 730 ion exchange resin. The extraction effectiveness of the resin is studied by using breakthrough curves. The experimental and simulation results were compared. A numerical model is proposed for the investigation of the ion exchange phenomenon using gPROMS using various optimized parameters like flow rate, bed height, and initial concentration of wastewater containing Cu (II) heavy metal ion in the column. For instance, the effects of flow rate, bed height, and inlet concentration of heavy metal on a breakthrough curve are investigated in depth. The results illustrate that the predicted theoretical breakthrough curves show analogous patterns with the corresponding investigational output with a discrepancy of the equilibrium time. The predictions of the model will help to discover the optimal conditions of operation.

Keywords: Adsorption, Breakthrough curve, gPROM, Modeling, Simulations

The Indion 730 is the most commonly used polystyrene cross-linked resin, which consists of a sulphonic functional group. This resin has high resistance towards stress-strain and shows superiority in processing organic as well as inorganic material removal. Many industries use heavy metals in processing, such as the textile industry, mining industry, ceramic industry. The traces of heavy metals in the effluent of such industries are harmful to the environment as well as human health[1]. The association of these heavy metals in the food chain has affected the biological systems. Some of these metals are essential for life, such as copper in the form of micronutrients are essential for a healthy metabolism, healthy bones, and the nervous system. However, higher levels are harmful to plants, animals, and humans as they tend to accumulate in the bodies. The maximum concentration of copper acceptable in drinking water is 1.3 mg/L[2]. Though it is acceptable with some limited concentration in drinking water, there is a need to remove the higher deposition of Cu in wastewater to avoid the dreadful effects of copper on the environment as well as humans. The harmful effects include dreadful effects on the kidneys, brain, liver, and eyes of humans and animals, while excessive copper toxicity in pants causes a restriction in the growth of the roots, reduced seed germination, and low shoot vigor. Hence it is necessary to remove Cu from Acid Mine drainage AMD for prevention from its ill effects. Since the past few years, the development of the removal of these heavy metals and the development of a low-cost solution has been studied. For e.g., the use of adsorbent rice husk[1], Flyash[3], modified sawdust[4], groundnut shell[5], and many more[6]. The mining industry across the world in the form of AMD induces water pollution. During the excavation of minerals like sulfide/pyretic, environmental exposure provokes the formation of acids and various unwanted reactions. These acids and heavy metals are byproducts of the mining industry and are mostly released in drainages. These effluents from the drainages with the conventional wastewater treatment processes were found to prominent release of the various complex effluents of high acidity and toxicity. In addition, AMD also has additions from the mill tailings, which makes the effluents more complex for the treatment with conventional methods[7]. The variations of *p*H, ion concentrations, metal-oxide presence, acid concentration, and heavy metal composition are the prominent parameters that distinguish the AMD for further treatment[8]. The toxicity due to heavy metals associated with AMD specifically has a great concern when we deal with environmental issues on priority[9]. The conventional treatments for the removal of heavy metals are precipitation methods, adsorption, chemical treatment, etc. were studied widely in literature, and it is found that the ion-exchange method has promising advantages over all the effective methods[10]. The ion exchange systems for ADM are customary in the modern effluent treatment of the mining industry[11]. The chemical treatment of the AMD discharge needs a continuous process to handle the large quantity of output within a stipulated time. The packed bed column was the best suitable solution where the resins are filled in the appropriate arrangement, and the discharge from AMD follows through the column. The basic requirement of this chemical ion-exchange process is an appropriate design of the packed bed column, fixing the input and out parameters like flow rate, pressure drop, initial concentrations, and many more. However, the types of resin, packing arrangements, the pressure drop across the packing, and adsorption isotherm are also important parameters in the design of the packed bed column[10]. One can divide these parameters into two different groups as process parameters and design parameters. The process parameters have major importance for the design of an ion exchange system. The majority of the large-scale processes use comparatively substantial permeable particles to decrease pressure drop and adsorbent price. The pressure drop across the resins affects the diffusion rate of the ions across the fluids and the interphase. This diffusion rate of ions in the fluid and at the interface of solid and fluid is the rate-limiting step of the process, and this is also responsible for the shabbiness in breakthrough curves of the ion exchange process[12].

The other important parameter which alters the diffusion mechanisms was the pore volume associated with the resins. The fluid flowing through the resin walls works as a micro filter and allows only selective ions to pass, where the remaining get adsorbed on the wall surface of the pores. The pore diffusion occurs along the walls of the pore, and its volume significantly affects the rate of diffusion[13]. The affinity of ions also affects the rate of diffusion; in general lower the affinity of a solute lowers the diffusion rate. In the interphase diffusion mechanism, the affinity of the solute is always low towards the new phase[14]. Thus, the effect of the affinity of ions can be neglected, and the predominant pore diffusion model was used for the forecasting of the kinetics of ion exchange[15-16].

In the present work, the experimental results of the adsorption column are correlated with the results of gPROM, the next-generation modeling tools to understand the process cycle. The effect of different concentrations, the height of the bed, and the flow rates on adsorption breakthrough curves have been evaluated and discussed. The results discussed here are significant to introduce new directions for modeling and simulation research in the future.

Experimental Section

Indion 730 resin sample

The anion exchange resins *Indion 730* (Ion Exchange India Limited, India) is used for the removal of heavy metals from acid mine drainage wastewater. The physical properties and specifications of the resin are reported in Table 1.

The following chemicals have been used in the removal of Cu (II) Ions experiments. $CuSO_4 \cdot 5H_2O$ (AR grade; Loba Chemie), H_2SO_4 (AR grade), NaOH (AR grade). All the chemicals used in the experiment were used as received without any further purification or pre-treatment.

Preparation of heavy metal solution

Aqueous stock solutions (1000 mg/l) of Cu (II) were prepared using salts of $CuSO_4 \cdot 5H_2O$. The concentration ranges varied between 100 to 200 mg/**l** for a single metal aqueous solution. To assess the effect of *p*H on the removal of Cu (II) Ions, the experiments were carried out with different *p*H ranges. The *p*H of the solution was adjusted with dilute 0.1 N H_2SO_4 or 0.1 N NaOH.

Table 1 — Model parameters value for simulation

Parameters	Values
Bed height	60 cm
Column radius	5 cm
Pellet radius	0.3 cm
Pore diffusivity, *Dp*	2.5×10^{-7} cm^2/s
Mass transfer coefficient, k_f	1.5×10^{-4} cm/s
Axial Dispersion Coefficient, D_L	5.9×10^{-6} cm^2/s
Bed porosity	0.44
Pellet porosity	0.55
Density of particle	1446.8 kg/m^3
Density of bulk fluid liquid	1 gm/cm^3
Langmuir constant ,b	0.958 for Indion 730
Maximum adsorption capacity,q0	1.7 meq / ml for Indion 730

Column studies

A glass column with an inner diameter of 50 mm and a height of 1000 mm was used to carry out the experiments. The column was packed with the Indion 730 resins at the height of 60 cm. The resin was cautiously positioned in the column to avoid the detention of air among the particles, which made the bed additional compacted. The experiments were performed at room temperature (i.e., 32°C) with varying the initial concentration of Cu (II) and flow rate of the solution through the column, i.e., 100, 150, 200 mg/L and 5, 10, and 15 liters per hour (lph), respectively. To monitor the concentration of Cu (II) in the effluent, an aliquot of the reaction mixture was withdrawn and measured at chosen time intervals. The process was stopped when the inlet and outlet concentration of Cu (II) became equal.

Analysis

The Cu (II) ion concentration in the reaction mixture was determined by UV-Visible spectrophotometer (Make: Chemito; Model: AA 201) at λ= 336 nm. To minimize the error due to reflected light, the blank solution was put in a cuvette and read as a reference sample. The blank solution was prepared in milli-Q water without the addition of the pollutant, i.e., Cu (II) ions. The analytical wavelength was set by using the most concentrated working standard. The calibration curve was prepared using the different concentrations of Cu (II) and Absorbance (A). A sample of unknown concentration was calculated with the help of the calibration curve.

Mathematical modeling and simulation for dynamic study

In the proposed system, the convection in the axial direction across the length of the column and the mass transfer through axial dispersion have a greater impact on the ion exchange process. Bautista et al. (2003) reported the kinetic model for the amylose from aspergillus oryzane. The kinetic model which they proposed considers mass transfer resistance, both internal and external. The following assumptions are used in this study:

1. Isothermal conditions are throughout the operations.
2. Langmuir isotherm was used to describe the equilibrium of adsorption.
3. The liquid velocity varies in the length of the column.
4. Fick's law diffusion is obeyed by the intraparticle mass transfer, and its characterized by the pore diffusion coefficient, D_P.
5. Mass transfer across the boundary layer surrounding the solid particles is characterized by the external-film mass transfer coefficient, k_f.
6. Spherical resins particles are uniform in size and density.

The schematic representation of a section of the packed bed is shown in Fig. 1. The basic solute balance for a section (dz) of the bed was helpful for the model preparation. The input and output flow difference is associated with the rate of accumulation of solute. The change in superficial velocity is neglected while developing the model.

$$-D_L\frac{\partial^2 C_b}{\partial Z}+V\frac{\partial C_b}{\partial Z}+C_b\frac{\partial V}{\partial Z}+\frac{\partial C_b}{\partial t}+\rho_p\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial q_p}{\partial t}=0 \qquad \ldots(1)$$

The initial conditions are as follows:

$$_b = C_{b0} \text{ z = 0, t = 0} \qquad \ldots(2)$$

$$C_b = 0 \; 0 < z \le L, \text{ t = 0} \qquad \ldots(3)$$

The following equations give the conditions at the entrance and exit of the column.

$$D_L\frac{\partial (C_b)}{\partial Z}=-V_0(C_{b0}-C_b)\text{, z = 0, t > 0} \qquad \ldots(4)$$

$$\frac{\partial C_b}{\partial Z}=0\text{, z = }L\text{, t}\ge 0 \qquad \ldots(5)$$

The following equation was used to guess (dV/dz). Suppose the liquid density was constant, then the total mass balance gives,

$$\rho_1\frac{\partial V}{\partial Z}=-(1-\varepsilon)\rho_S\frac{\partial q_p}{\partial t} \qquad \ldots(6)$$

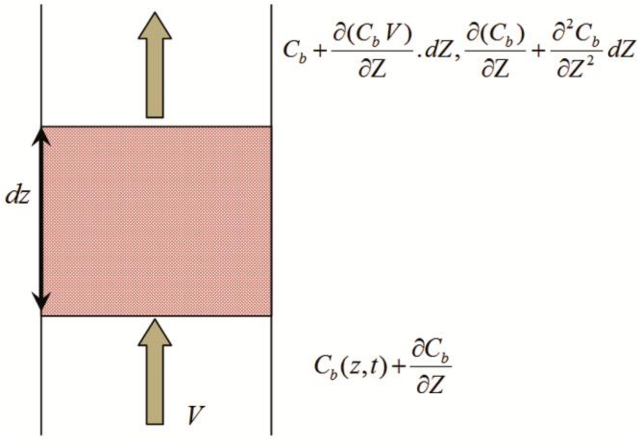

Fig. 1 — Mass balance across the section of packed bed

Velocity boundary conditions are defined as:

$$V = V_0,\ z = 0,\ t > 0 \qquad \ldots(7)$$

$$\frac{\partial V}{\partial Z} = 0,\ z = L,\ t > 0 \qquad \ldots(8)$$

The inter-phase mass transfer rate may be stated as:

$$\rho_s \frac{\partial q_p}{\partial t} = \frac{3K_f}{a_p}\left(C_b - C_s\right) \qquad \ldots(9)$$

Diffusion plays an important role in mass transfer through the pores. The overall conservation equation is specified as:

$$\varepsilon_p \frac{\partial C}{\partial t} + \left(1-\varepsilon_p\right)\rho_p \frac{\partial q}{\partial t} = D_p\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right) \qquad \ldots(10)$$

Assuming immediate balance

$$\frac{\partial q}{\partial t} = \frac{\partial c}{\partial t}\frac{\partial q}{\partial c} \qquad \ldots(11)$$

Subsequently**,** reshuffling equation (3)

$$\frac{\partial q}{\partial t} = \frac{1}{\left[1+\rho_p\left(\frac{1-\varepsilon_p}{\varepsilon_p}\right)\frac{\partial q}{\partial c}\right]} D_p\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right) \qquad \ldots(12)$$

Consider the following initial conditions

$$C = 0,\ q = 0,\ 0 < r < a_p,\ t = 0 \qquad \ldots(13)$$

The balance condition and continuity condition on the exterior surface of the resins are conveyed as:

$$\frac{\partial q}{\partial t} = 0,\ r = 0,\ t > 0 \qquad \ldots(14)$$

$$K_f\left(C_b - C_S\right) = D_p\frac{\partial c}{\partial r},\ r = a_p,\ t > 0 \qquad \ldots(15)$$

The process was illustrated by Langmuir isotherm and was nonlinear

$$q = \frac{abC}{1+bC} \qquad \ldots(16)$$

Simulation

The equations 1 to 16 are solved by the finite difference method as nonlinear adsorption equilibrium is considered. A gPROM (v.6.1) software was used to solve the mathematical equations. The algorithm is shown in Fig. 2. The parameters utilized for simulation in the present study are given in Table 1.

Results and Discussion

The proposed study of the removal of heavy metal from the wastewater helps for the development of the process model. The outlet concentration maintenance with a discrete operation system and corresponding control action is a bottleneck for the mining industry. The present model provides a solution for the discrete operating system. The variation of bed height with the linear velocity variation is considered during the modeling of the process, and corresponding results are compared with the actual experimental outcomes. The difference between the observed experimental value and the predicted value of the model is noted as an error associated with the prediction of the model.

The results from Fig. 3 show that the breakpoint is attained earlier. The incisive breakthrough curve was observed to reach equilibrium at a certain time. The outcomes observed with the adoption system are acceptable and obey the fundamentals of the processes. The velocity of fluid shows significant variation as it travels through the bed length; this is due to the resistance and drag offered by the resin packing. This variation in the kinetic velocity of losses offers the additional contact sites of the solid-liquid phase inside the bed, also enhances the mass transfer flux, and helps to overcome the pore resistance associated with the resin. The mass balance fundamental equation proves the variation of velocity, as noted in Eq. 6. This shows that the effect of the initial flow rate on the breakthrough curve was noteworthy. The proposed mathematical model simulates with the help of gPROMS, and the study

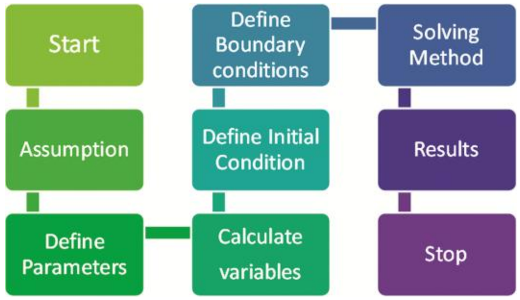

Fig. 2 — Algorithm for the investigation on the column performance of Cu (II) removal by adsorption in a fixed bed.

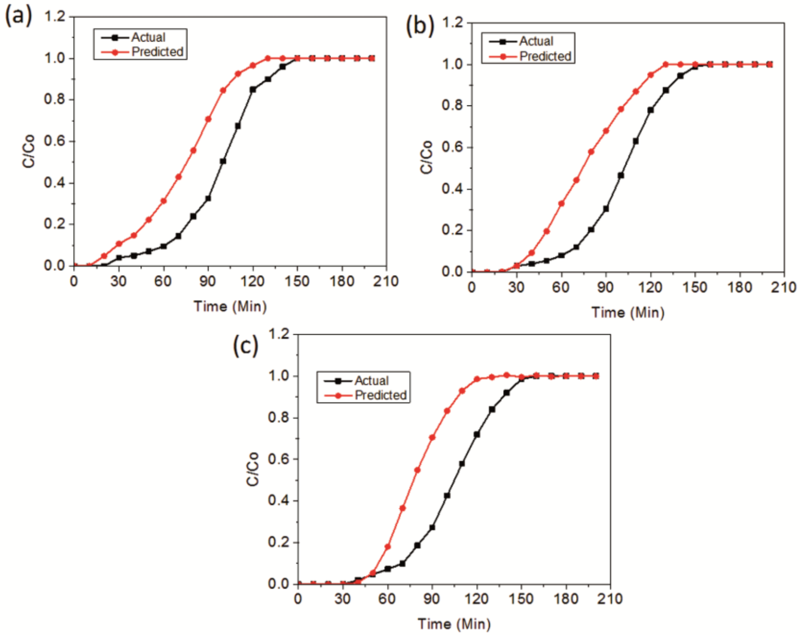

Fig. 3 — Effect of flow rate on outlet metal concentration (a) 5 lph; (b) 10 lph; (c) 15 lph.

has been noted with variations such as flow rates, initial concentration of heavy metals, initial *p*H of stream, and design parameter bed height.

Effect of flow rate on the removal of heavy metal

The initial flow rate of the stream in the packed bed column significantly affects the initial and final concentration of heavy metal in wastewater. In the present study, three different flow rates were studied. The observations of the experiment at individual flowrate were mapped out in Figure 3a-c for the constant bed thickness of 60 cm. The inlet stream concentration was kept constant (200 mg/l). The observation of the outlet concentration at different flow rates was confirmed with repetitive analysis until three same consistent results. The flow rates, such as 5 lph, 10 lph, and 15 lph, are used for the study.

As seen from Fig. 3, it is noted that as the flow rate increases from 5 to 15 lph, the breakthrough curve becomes vertical. The breakpoint of time decreases from 50 to 20 min. This shows that as the flow rate increases, the metal concentration ratio (*C/Co*) increases, and the breakpoint decreases. The residence time of heavy metal ions was reduced since the flow rate was increased from 5 lph to 15 lph. Insufficient residence time is the main cause due to which the packed column cannot attain equilibrium at a higher flow rate. This phenomenon results in a heavy release of metal ions in the outlet stream, and the efficiency of the packed bed column decreases. At the flow rate of 5 lph, the breakpoint time is 50 min, with a change in breakpoint time of 60%. It was noted that as the flow rate increases, the % error associated with the value prediction also increases simultaneously. The % error values were 0, 25, and 25 %, respectively for the flow rates 5, 10, and 15 lph.

Effect of bed height on the outlet concentration of metal

The effect of bed height on the removal of Cu (II) is depicted in Fig. 4a-c for flow rate 5 lph and inlet Cu (II) concentration of 200 mg/L. For the present study, the bed heights considered are 20, 40 and 60 cm. It was noted that the variation in design parameter bed height affects the exit concentration of the heavy metal ion. The effective space-time of the stream get increases, which leads to enhancement in breakpoint time from 20 to 50 min as the bed height increases from 20 to 60 cm. In addition, the bed is saturated in a lesser amount of time for smaller bed heights. Smaller bed height corresponds to a smaller quantity of resins, which affects the capacity for the bed to adsorb Cu (II) from solution, and a faster increase in the rate of Cu (II) adsorption is anticipated. For the bed height of 20, 40 and 60 cm, the breakpoint time is 20, 30 and 50 min, respectively. For the bed height 20, 40 and 60 cm, the percentage error is 33, 0 and 0 %, respectively.

Effect of Inlet concentration

Fig. 5a-c demonstrated the influence of inlet Cu (II) concentration on absorption capacitance of the process through effluent concentration correlations.

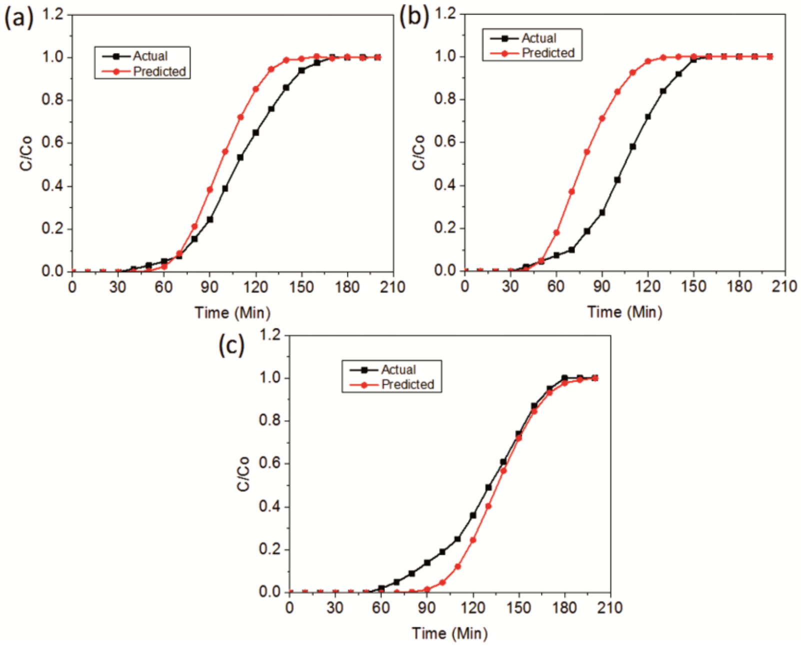

Fig. 4 — Effect of bed height on a breakthrough curve (a) 20, b) 40, and (c) 60 cm actual and predicted values.

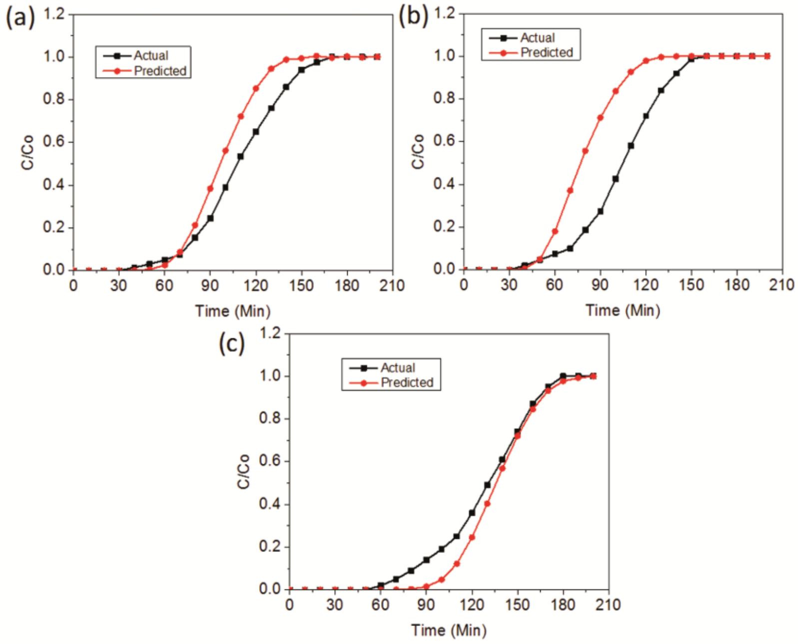

Fig. 5 — Influence of inlet Cu (II) concentration on breakthrough curve as (a)100 mg/L, (b) 150 mgL, and (c) 200 mg/L

The inlet concentration of Cu (II) is considered as 10, 150 and 200 mg/L for the study. The inlet concentration varies with the experiment; however, during this study, the bed height and the flow rate are kept constant. The results observed that as the inlet Cu (II) concentration increases, the breakpoint time of the process reduces. Eventually, it was found that as the Cu (II) concentration increases in the inlet, the breakpoint is achieved with minimal time. At the initial concentration of Cu(II) 100 mg/L, the breakpoint was observed at 100 min, whereas with the higher concentration, it reduces to 40 min. The concentration significantly affects the absorption process, and the mass transfer flux plays an important role in it. At a lower concentration of Cu(II), mass transfer flux was poor due to the low concentration gradient. The induced driving forces through the pore due to the lower mass transfer flux are also eventually low. This leads to higher breakthrough time. Whereas, at a high concentration of Cu(II), all the conditions are reversed. The higher driving force at the pore leads to achieving the equilibrium early. The model predicted values show some slight error with the observed value. At higher concentrations, predictions exactly match with the higher concentration system. For the inlet Cu (II) concentration of 100, 150, and 200 mg/L the breakpoint time is 100, 60, and 50 min, and their corresponding error is 30, 0, and 0%, respectively.

Conclusion

The mathematical model of a packed bed column of resin has been devised with consideration of exploitation Indion 730 commercial resin. The variation in input conditions such as flow rate and *p*H of the stream has been studied with noted variation in outlet concentration of heavy metals. However, the design parameter bed height also significantly affects the outlet concentration of heavy metals. The model includes all the possible affecting parameters such as the mass transfer coefficient of interface film, pore diffusion resistance, etc., which can show the variation due to slight changes in input parameters. The breakthrough curves noted meaningful variation as the initial concentration, flow rate, and pH variations in the input stream from AMD. The breakthrough time gets reduced, and the leaving stream will not get sufficient time to achieve equilibrium; this leads the existing stream with a higher concentration of heavy metals. The vertical nature of the breakthrough curve proves the same condition. The Cu (II) concentration ratio increases more rapidly for a higher bed height than for a smaller bed height, sharp breakthrough curves are found, and breakpoint time is achieved shortly for larger feed concentration. The formulation of the mathematical model for Cu (II) by ion exchange and simulation of the same using gPROMS shows that there is a close correspondence between experimental and simulated data. Hence, it is clear that the model is well fitted for the said phenomena. These results develop the recognition of ion exchange phenomena regarding pore diffusion and are very functional in the creation of ion exchange beds to treat acid mine drainage wastewaters.

Nomenclature

a_p	radius of the resin, m
A	cross section area, m^2
B	Langmuir isotherm parameter, ml/mg
c	solute concentration in the liquid phase inside the pores, mg/l
C	bulk phase metal concentration, mg/ml
C_s	liquid phase concentration in equilibrium with *q*s on the surface, mg/ml
C_o	inlet CU (II) concentration, mg/ml
D_L	axial dispersion coefficient, m^2/s
D_p	pore diffusion coefficient, m^2/s
k_f	external film mass transfer coefficient, m/s
L	column length, m
Q	average adsorbed phase dye concentration, mg/g
q_m	Langmuir isotherm parameter, mg/g
q_s	Concentration on the surface of the pellet, mg/g
Q	flow rate, ml/min
r	radial coordinate, m
t	time, sec
V	superficial velocity, m/s
V_o	initial superficial velocity, m/s
V_i	interstitial velocity inside the bed, m/s
z	axial coordinate, m

Greek letters

ε	bed porosity
ε_p	porosity of the resin pellet
l	solution density, kg/m^3
p	particle density, kg/m^3
b	bed density, kg/m^3

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