International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.10 No.5, pp 664-673, 2017

Column performance evaluation and hydrodynamic modeling studies for the removal of copper and cadmium using mixed adsorbent in continuous packed bed reactor

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Abstract : Experiments were conducted to investigate the copper and cadmium removal from the aqueous solution by the mixed adsorbent prepared by blending activated charcoal and bone charcoal in 1:1 ratio. Approximately above 99% of the copper and 95% of the cadmium ions originally present in the solution were adsorbed onto the mixed adsorbent. The experimental data obtained proved that the effect of bed weight, volumetric flow rate and inlet (initial metal ion) concentration plays a significant role on the removal of Cu (II) and Cd (II).The operation and behavior of the continuous column adsorption can be determined by using the time to reach breakthrough and the shape of the breakthrough curve.The bed height of 36 cm, 10ml/min for both copper and cadmium offered optimum breakthrough curves and indicates that the higher performance of column. The basic hydrodynamic parameters of the packed bed were analyzed. The influence of different parameters such as liquid velocity, particles size and voidage on mass transfer in packed bed was represented. The regression analysis was carried at different flow rates and the regression or correlation coefficient R^2 values are very close to 1 which indicates that the column hydro dynamics better fits the adsorption system.
Keywords : Mixed adsorbent, bed weight, volumetric flow rate, Initial metal ion concentration, break through curve, Hydro dynamic parameters, Correlation coefficient.

1. Introduction

The contamination of surface waters by heavy metal ions has become a serious ecological issue and health problem due to their toxic effect even in low concentrations. Heavy metals are of special concern because they are non-degradable and thus persistent. Heavy metal ions such as cobalt, copper, chromium, nickel, palladium, lead, zinc are detected in the waste streams from the mining operations [1], tanneries [2], electronics [3], electroplating, batteries [4] and petrochemicals [5] industries has major effects on the human and aquatic life [6].

Water pollution remains a major problem in the environment due to the development of urbanization and industrialization which have contributed to the large scale of pollution for both human and aquatic life. The wastewater is discharged into the streams. Wells, Rivers and other water bodies without proper treatment. The pollution depreciates the land values, increases the municipal cost, operational cost and cause adverse biological and human health effects. Heavy metals are non-biodegradable in nature and cause and their presence in the water streams leads to bioaccumulation in living organisms causing health problems in animals, plants and human life [7]. Industrial effluents containing enormous quantities of inorganic and organic chemical wastes, which are steadily become more difficult to treat by ongoing conventional methods.

A number of conventional treatment technologies such as Chemical precipitation, ion exchange, electro dialysis, membrane separations, reverse osmosis, and solvent extraction and adsorption have been considered for treatment of wastewater contaminated with organic substances. Among them adsorption is found to be the most effective method [8]. Adsorption is found to be superior to any other treatment methods because of the simplicity of design, ease of operation, capability for adsorbing a broad range of different types of adsorbate concentrations efficiently. Commercial activated carbon is regarded the most effective material for controlling the organic load [5]. Adsorption denotes to the separation of solute particles in a confined space from a liquid phase (fluid phase) on to solid surface. The particle of the adsorbate comes from the fluid segment into the boundary, the place they persist for an interval of phase. In a rescindable method, the particles return to the segment from which they got here or reversibly cross into an alternative segment even as other particles exchange them at the boundary. On accomplishment of the solid surface, the adsorbed particles interchange energy with structural atoms of the outside surface and if enough period was once there for adsorption, the adsorbed particles and the surface atoms reach thermal stability .The quantity of molecules entering on the boundary in a assumed period is equivalent to the number of molecules parting the boundary to go into the fluid segment [9-10].

1.1 Break through Curves

The performance of a fixed-bed column was described through the concept of the breakthrough curve. The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of an adsorption column. The loading behaviour of metal ion to be adsorbed from solution in a fixed-bed is usually expressed in term of C_e/C_o as a function of time or volume of the effluent for a given bed weight giving a breakthrough curve.

In any case, the performance of an adsorption treatment mainly depends on the thermodynamic aspects of solute-solvent-sorbent interactions and on the transport phenomena involving the diffusive-convective transport within the porous media [11,12]. In a fixed-bed device, the contaminated water is introduced in a clean bed of mixed adsorbent from the top of the column and pollutant removal occurs in a narrow band at the top of the column, referred to as mass transfer / exchange zone (MTZ). As operation proceeds, the upper layers of blended adsorbent get to be saturated (soaked) with solute and the adsorption zone moves downwards until bottom of the column is reached. Under these conditions, the solute concentration in the effluent begins to increase. The MTZ extent mainly depends on liquid-solid relative velocity, and on the adsorbent properties (particle diameter, micro porous structure). The higher the MTZ extent the lower the efficient use of the adsorbing bed. Experimental dynamic tests showed that an increase in initial concentration and the liquid flow rate leads to shorter breakpoint time; moreover, the breakthrough curves become steeper as a consequence of higher velocity that enhances the external mass transport. The plot between the ratio of logarithm of equilibrium outlet concentration to the initial concentration of the metal ion, gives a relation between $\ln(C_e/C_o)$ vs reaction time in terms of various linear models (by various parameters) and predicts the nature of the adsorbent-adsorbate system are called Break through curves. They depends on the effect of volumetric flow rate, weight of the adsorbent packed at different bed weights and initial metal ion concentration of the metal ion solution. The study of variation of flow rate with bed weight at a fixed initial concentration of 100 ppm gives the concentration ratio profile with respect to outlet effluent sampling time (min).

In this paper a systematic and detailed study have been carried out to know the column performance calculations in terms of % removal, breakthrough time and saturation time, sorption exhaustion rate and empty bed contact timefor the removal of Cd (II) and Cu (II) using mixed adsorbent prepared by mixing Activated charcoal and Bone Charcoal (1:1 ratio) in continuous flow operation. The hydro dynamic data for mass transfer in this paper were shown using various dimensional numbers such as Sherwood number (Sh), Schmidt number (Sc), Mass transfer coefficient (k) and Colburn factor (J_D). The plot between Reynolds number (Re) and the ratio of Sh/Sc were represented at different flow rates with higher R^2 values.

2.Materials & Methods

All the chemicals including adsorbents used for the studies were purchased from Sigma Aldrich, India and have purity above 99.5 %. All the reagents, buffer solutions used for the study were Analytical grade.

2.1 Methods

Atomic Absorption Spectrophotometer (Thermo Scientific ICE 3000 series) used to analyze Cu (II) & Cd (II) before and after adsorption.

2.1.1 Preparation of the mixed adsorbent

The mixed adsorbent was prepared in 1:1 ratio and sieve analysis (SELEC XT 264, AIMIL company ltd) was carried out in a rotary sieve shaker to determine the particle size of the mixed adsorbent. The average particle diameter of the mixed adsorbent was obtained as 572.2 nm (Nano meters).

2.1.2 Column Studies

Continuous flow operation experiments were conducted in a transparent cylindrical plastic column (4 cm internal diameter and 100 cm height). A 20 mesh size stainless sieve was attached to the bottom of the column. A known quantity of the adsorbent in the ratio of 1:1 (mixed adsorbent) was added in the column to yield the desired bed height (12cm, 24cm, 36cm). Cu (II) and Cd (II) solution of known concentration (100 mg/l was pumped into the column using a 40 W submersible pump at the desired flow rate (10ml/min, 20ml/min, 30ml/min). Samples were collected from the exit of the column at different bed heights and at different intervals of time until the achievement of equilibrium and analyzed using Atomic Absorption Spectrophotometer (AAS).

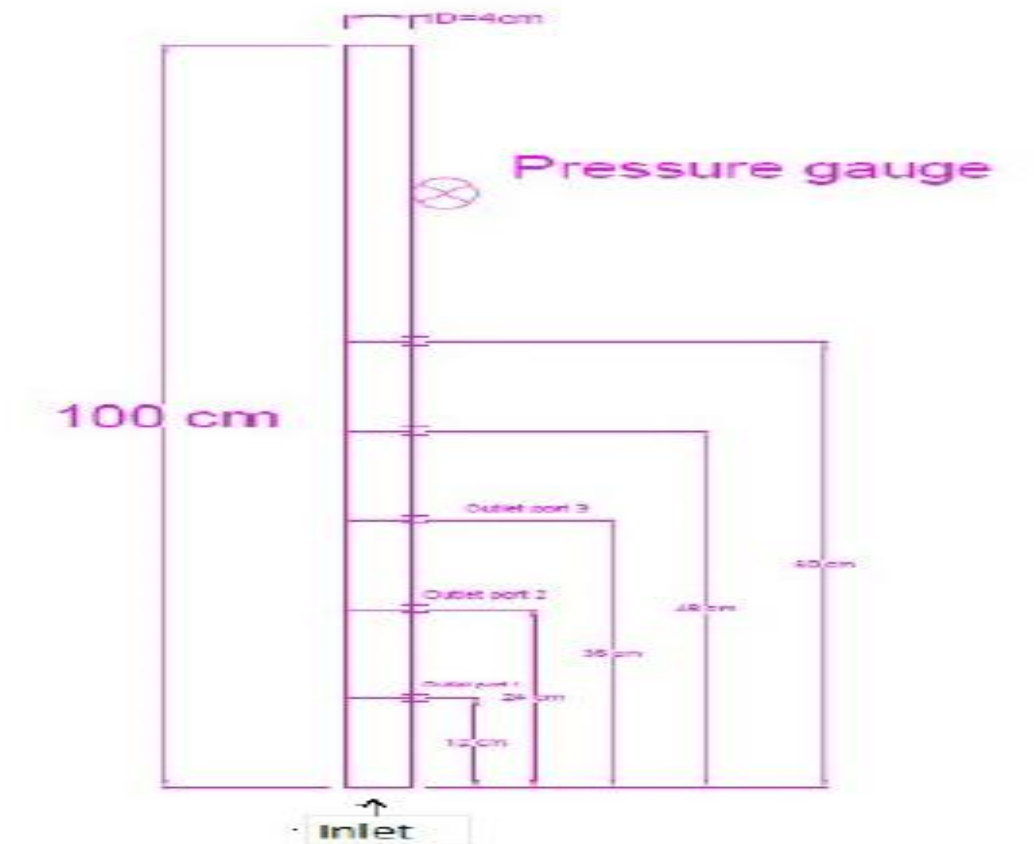

Fig 1 Laboratory Experimental setup of Continuous flow column

2.1 Parameters & Dimensions of the packed bed column

Weight of the mixed adsorbent added 50g, 100g, and 150g respectively (for 12 cm -25 g each; for 24 cm -50 g each; for 36 cm -75 g each.)

Inner Diameter of the column: 4cm
Bed height studied = 12, 24, 36cm

Total height of the column =100cm
Adsorbent ratio = 1:1(AC+ BC)
Submersible pump used for sending the effluent into the column = 40 Watts.
Initial Metal Con of the metal ions Cu and Cd (C_o) = 100 ppm
Effect of volumetric flow rate -10, 20, 30 ml/min
Effect of Weight of the adsorbent (bed height) -12cm, 24cm, 36cm

3. Results and Discussion

3.1 Study of bed heights (weight of the adsorbent) and volumetric flow rate

The design of the packed bed column has been studied at a bed height of 12 cm, 24 cm, 36 cm and by flow rates varying from 10, 20, 30 ml/min with an initial concentration of 100 ppm. The main design of the column involves the study of break through curves experimentally with the effect of bed height and volumetric flow rate.The results were compared between the industrial and synthetic solution data in terms of % removal, breakthrough time and saturation time, sorption exhaustion rate, empty bed contact time, volume treated at break through point (ml) and saturation point (ml) in order to evaluate the column performance.

3.1 Column Performance Evaluation

The efficiency of the continuous column performance can be determined by using the time to reach breakthrough and the shape of the breakthrough curve. The breakthrough curves show the loading behavior of a metal ion in a continuous column [13] and are usually expressed in terms of normalized concentration defined as the ratio of the outlet concentration (C_t) to the inlet concentration (C_o) as a function of time (in minutes) [14]. The total metal adsorbed, m_{ad}(g), in the fixed bed column can be calculated from the area under the curve multiplied by the flow rate from **Eq.1**whichis given as follows:

$$M_{ad} = \frac{Q}{1000}\int_{t=0}^{t=total} C_{ad}\, dt \quad (1)$$

The uptake capacity (q_e) by the adsorbent for synthetic solution was shown in **Eq. 2** given as

$$q_e = \frac{M_{ad}}{M} \quad (2)$$

whereq_e is the adsorbent uptake capacity (mg/g), M_{ad} is the metal ion adsorbed (g) and M is the adsorbent mass (g). The total amount of metal ion sent through the column was calculated by **Eq.3** given as

$$m_{total} = \frac{C_O\, F\, t_e}{1000} \quad (3)$$

where C_o is the inlet concentration of metal ion (mg/L), F is the flow rate of metal ion solution (mL/min), and t_e is the exhaustion time (minutes). The % removal of metal ions (columnperformance) was calculated by**Eq. 4** given as

$$\text{Total \% removal} = \frac{m_{ads}}{m_{total}} \times 100 \quad (4)$$

Empty bed contact time / Empty bed residence time is the time required for the liquid/ fluid to fill the empty column and is defined by **Eq. 5** as

$$\text{EBCT or EBRT} = \frac{Empty\ bed\ volume\ (ml)}{volumetric\ flow\ rate\ of\ the\ fluid\ (\frac{ml}{min})} \quad (5)$$

The rate of exhaustion (AER, g/L) [33] was defined as mass of sorbent deactivated per unit volume of watertreated at the breakthrough point and was calculated by the following **Eq. 6** given as

$$\textbf{Sorbent usage rate or Adsorbent exhaustion rate} = \frac{Mass\ of\ the\ adsorbent\ \ in\ the\ column}{volume\ trated\ at\ the\ break\ through\ point\ (L)}$$

or also defined by **AER** = $\frac{mass\ of\ the\ sorbent\ (g)\ in\ the\ column}{volume\ of\ water\ treated\ (L)}$**(6)**

3.3 Effect of flow rate

Experiments were carried out by varying the flow rate of synthetic solution between 10-30 ml/min. The adsorption column data were summarized in **Tables 1 and 2**for copper and **Tables 3 and 4**for cadmium, respectively. It was observed that with an increase in flow rate from 10 to 30 ml/min at 12 cm bed height both the breakthrough time and saturation time decreased from 50 to 20 min and 400 to 200 min respectively for copper, and breakthrough time and saturation time decreased from 50 to 15 min, and 180 to 80 min for cadmium, respectively.

The same pattern was followed for 100 g and 150 g at different flow rates for both the metals. With the increase of flow rate from 10 ml/min to 30 ml/min at 24 cm bed height (100 g), the breakthrough time and saturation time decreased from 60 to 40 min and 450 to 250 min respectively for copper, the breakthrough time and saturation time decreased from 35 to 25 min and 320 to 150 min respectively for cadmium. Similarly with the increase of flow rate from 10 ml/min to 30 ml/min at 36 cm bed height (150 g), the breakthrough time and saturation time decreased from 65 to 50 min and 600 to 350 min respectively for copper, the breakthrough time and saturation time decreased from 60 to 30 min, and 450 to 200 min, respectively for cadmium. The removal efficiency of the mixed adsorbent substantially decreased with an increase in flow rate at different adsorbent dosage of 50, 100, and 150 g respectively for both the metals. This can be attributed to the fact that at lowest flow rate, the residence time of Cu^{2+} and Cd^{2+}ions in the column increases and as result the Cu^{2+} and Cd^{2+} ions have more time to diffuse into the pores of the mixed adsorbent through intra-particle diffusion resulting in a longer breakthrough time and saturation time as well as more amount of metal adsorption takes place which enhances the % removal[15].

3.4 Effect of bed height

The removal of Cu^{2+} and Cd^{2+} ions at different bed heights were studied at 100 ppm metal ion concentration and fixed flow rate of 10ml/min. With the increase in bed height, the removal efficiency, breakthrough time and saturation time, sorbent exhaustion rate (SER) increases as shown in **Tables 2 and 3**for copper and cadmium respectively. The increase in removal efficiency of Cu^{2+} and Cd^{2+} ions by the mixed adsorbent was due to the availability of higher number of adsorption sites and increase in the volume of effluent. The empty bed contact time (EBCT) also increased from 15 to 45 min for both the metals. These observations suggest that the bed height of 36 cm, 10 ml/min offered optimum breakthrough curves for both the metals with highest % removal[15].

Table 1 Column Performance calculations for copper removal at different bed heights and adsorbent dosage for synthetic solution

Ads dosage (g)	Bed heights (Cm)	Volumetric flow rates (ml/min)	IMC	Break through time (min)	Saturation time(min)	Voltreated at breakthrough point (ml)	Vol treated at saturation point (ml)
50	12	10	100	50	400	500	4000
50	12	20	100	30	270	600	5400
50	12	30	100	20	200	600	6000
100	24	10	100	60	450	600	4500
100	24	20	100	50	370	1000	7400
100	24	30	100	40	270	1200	8100
150	36	10	100	65	600	650	6000
150	36	20	100	55	490	1100	9800
150	36	30	100	50	350	1500	10500

Table 2 Parameters of the fixed bed column for the removal of Cu^{2++} ions by the mixed adsorbent for synthetic solution

Ads dosage (g)	Bed heights (Cm)	Volumetric flow rates (ml/min)	IMC	M_{ad} (g)	m_{total}(g)	Total % removal	EBCT (min)	SER (g/dm^3)
50	12	10	100	248.5	400	62.13	15	497
50	12	20	100	257.77	540	47.73	7.5	429.61
50	12	30	100	269.67	600	44.95	5	449.45
100	24	10	100	303.51	450	67.45	30	505.86
100	24	20	100	356.84	740	48.22	15	356.84
100	24	30	100	376.92	810	46.53	10	314.1
150	36	10	100	469.46	600	78.24	45	722.24
150	36	20	100	544.23	980	55.53	22.5	493.61
150	36	30	100	582.48	1050	55.47	15	388.32

Table 3 Column Performance calculations for cadmium removal at different bed heights and adsorbent dosage for synthetic solution

Ads dosage (g)	Bed heights (Cm)	Volumetric flow rates (ml/min)	IMC	Break through time (min)	saturation time(min)	Vol treated at breakthrough point (ml)	vol of sol treated at saturation point (ml)
50	12	10	100	50	180	500	1800
50	12	20	100	25	120	500	2400
50	12	30	100	15	80	450	2400
100	24	10	100	35	320	350	3200
100	24	20	100	30	220	600	4400
100	24	30	100	25	150	750	4500
150	36	10	100	60	450	600	4500
150	36	20	100	40	320	800	6400
150	36	30	100	30	200	900	6000

Table 4 Parameters of the fixed bed column for the removal of Cd^{2++} ions by the mixed adsorbent for synthetic solution

Ads dosage (g)	Bed heights (Cm)	Volumetric flow rates (ml/min)	IMC (ppm)	M_{ad} (mg)	m_{total}(mg)	Total % removal	EBCT (min)	SER SER (g/dm^3)
50	12	10	100	58.73	180	32.63	15	117.46
50	12	20	100	88.1	240	36.71	7.5	176.1
50	12	30	100	91.65	240	38.19	5	203.7
100	24	10	100	212.7	320	66.47	30	607.7
100	24	20	100	215.87	440	49.7	15	349.78
100	24	30	100	219.21	450	48.71	10	250.8
150	36	10	100	316.25	450	70.28	45	527.1
150	36	20	100	348.04	640	54.38	22.5	435.1
150	36	30	100	264.74	600	44.12	15	294.15

3.5 Hydro dynamic studies

The hydrodynamic behavior of metal ion solution in packed bed column combined with forced convective mass transfer has been studied with respect to dimensionless numbers such as Sherwood number (Sh), Reynolds number (Re), and Schmidt number (Sc), Chinton-Colbourn factor (J_D), mass transfer coefficient (k). The empirical correlations for the above mentioned dimensionless numbers have been shown in **Eqs. 7, 8, 9**respectively [16].

Sherwood number $Sh = J_D \, Re \, Sc^{1/3}$ **(7)**

$$\frac{Sh}{Sc} = \left[\frac{k\,\rho\,y}{Q}\right] Re \quad (8)$$

Schmidt number, $Sc = \frac{\mu}{\rho D_{AB}}$ **(9)**

Q = volumetric flow rate (10, 20, 30 ml/min)
Where density of metal ion solution, ρ = 1000 kg/m^3
Viscosity of water, µ = 0.01 kg/ m-s
Diffusivity of water, D_{AB} = 1.29 *10^{-9} m^2/s
ε, porosity of the bed = 0.67 (Particles are in fine powder and calculated after adsorption)
J_D = Chilton –Colubrn factor
k = mass transfer coefficient (m/s)
y = mass fraction of the adsorbent varying with respect to bed heights (y for 12cm = 0.166, y for 24cm = 0.33 and y for 36 cm = 0.5)

$$Re_P = \frac{D_P v \rho}{\mu} \quad (10)$$

Velocity of the fluid, $V = \frac{Q}{A}$ **(11)**

Mass flow rate of the fluid, $m = Q \times \rho$ **(12)**

Where Q is the volumetric flow rate of the fluid (ml/min) and ρ is the density of the metal ion solution

Relationship between Sherwood number and Reynolds number for particles (dissolution method) where $Re = \frac{Re_p}{(1-\varepsilon)}$, show good agreement with our experimental data. Re_p is called Reynolds number of the particle.

Correlations to find Chilton Coulbrn factor are given as [17]

$J_D = 5.7\,(Re)^{-1.22}$ **for** $1 < Re < 30$ **(13)**

$J_D = 1.77\,(Re)^{-1.56}$ **for** $30 < Re < 1000$ **(14)**

where J_D, k, ρ, and $y$are Clinton-Colbourn factor, mass transfer coefficient (m/s), density of solution, and mass fraction of the component, respectively. Finally mass transfer coefficient (k) is found by **Eq.8** after calculating the ratio of Sh/Sc (Sherwood number to Schmidt number). The hydro dynamic modeling data has been reported in **Table 5.**

3.5.1 Hydrodynamic studies at various flow rates and bed heights

The hydrodynamic behavior of fluid flow inside the column has been shown in **Table 5.**It became evident from the **Table 5**that the dimensionless parameters varied significantly with flow rate and bed height inside the packed bed column [18]. It can be observed that with the increase of flow rate there was a significant rise in the velocity of fluid inside the column which increases the Reynolds number.

The Schmidt number, Sherwood number, Colubrn factor (J_D) decreases in the order of bed height increase from 12 to 36 cm at a constant volumetric flow rates.

The Sherwood number decreased with the increase of flow rate from 10 ml/min to 30 ml/min. However, with the increase of bed height at fixed flow rate, there was a decrease in velocity of the fluid, Schmidt number, Sherwood number, Colubrn factor (J_D) and increase in the Reynolds number was observed. The decrease in the values of these forced convective (inter phase) mass transfer parameters was due to the path resistance posed by the particles of bed, and this resistance increased with the increase of bed height and reduced when the flow rate was high. Therefore, in the present investigation it was summarized that large flow rates and smaller bed heights rendered the minimum possible resistance for the transfer of metal ions from liquid phase to packed bed. **Fig.2**indicatethe plot between the Reynolds number (Re) and the ratio of Sh/Sc (Sherwood number to Schmidt number) at different flow rates. The trend lines are drawn along with correlation coefficient (R^2) values to represent the column dynamics. It can be observed from the **Fig.2** that at different flow rates the regression / correlation coefficient (R^2) values were very close to 1 which indicates that the column hydro dynamics gives best fit to the adsorption system.

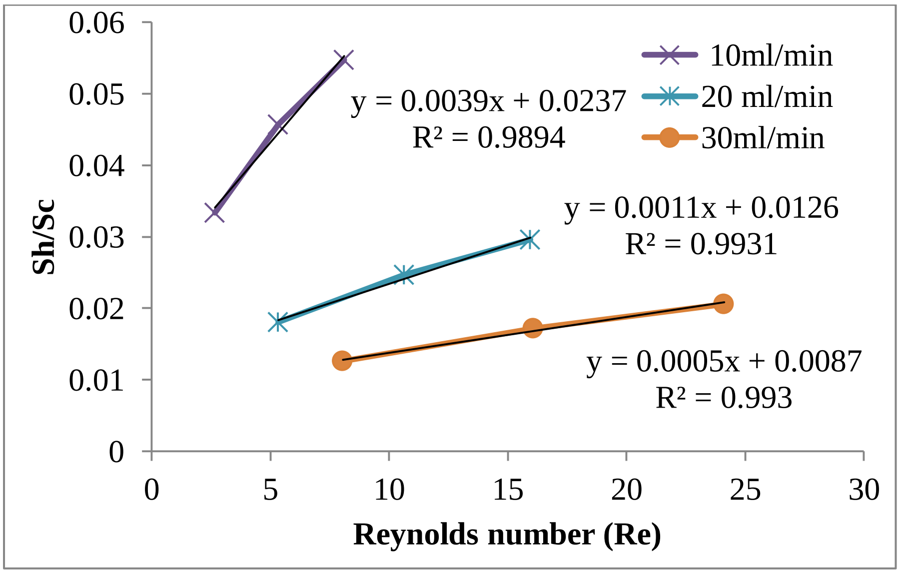

Fig 2:Plot between ratio of Sh/Scvs Reynolds number at different bed heights and volumetric flow rates representing the hydro dynamics.

Table 5 Hydro dynamic modeling of column studies at different flow rates and bed heights.

Flow rate	Bed height (Cm)	Re	Sc	Sh	Sh/ Sc	Colburn factor (J_D)	Mass fraction (y)	Mass transfer Coefficient ($K*10^{-12}$)
10ml/min	12	2.66	1550	51.91	0.0334	1.728	0.166	12.9
	24	5.32	775.2	35.15	0.0457	0.7417	0.33	4.33
	36	8.11	516.8	28.275	0.0547	0.443	0.5	2.25
20ml/min	12	5.32	3100.78	56.02	0.0181	0.7417	0.166	6.81
	24	10.64	1550.38	38.264	0.02468	0.318	0.33	2.34
	36	15.96	1033.6	30.61	0.0296	0.1941	0.5	1.236
30ml/min	12	8.04	4651.16	58.48	0.01257	0.4482	0.166	4.71
	24	16.08	2325.6	39.94	0.01717	0.1924	0.33	1.61
	36	24.12	1550.38	31.96	0.0206	0.1173	0.5	0.854

4. Conclusions

The operation and behavior of the continuous column adsorption can be determined by using the time to reach breakthrough and the shape of the breakthrough curve. The removal efficiency of the mixed adsorbent substantially decreased with an increase in flow rate at 12cm (50 g), 24cm (100 g),and 36cm (150 g) respectively. This can be attributed to the fact that at a lowest flow rate, the residence time of Cu^{2+} and Cd^{2+} ions in the column increases and as result the Cu and Cd ions have more time to diffuse into the pores of the mixed adsorbent through intraparticle diffusion resulting in a longer breakthrough time and saturation time. The bed height of 36 cm, 10ml/min for both copper and cadmium offered optimum breakthrough curves and indicates that the higher performance of column which further suggests that these studies can be extended to various industrial effluents containing complex heavy metals as well as to pilot plant studies.

The basic hydrodynamic parameters of the packed bed were analyzed. The influence of different parameters such as liquid velocity, particles size and voidage on mass transfer in packed bed was represented. The data for mass transfer in the investigated system were shown using Sherwood number (Sh), Schmidt number (Sc), mass transfer coefficient (k) and Colburn factor (J_D). The plot between Reynolds number (Re) and the ratio of Sh/Sc were represented at different flow rates. The regression analysis was carried at different flow rates and the regression or correlation coefficient R^2 values are very close to 1 which indicates that the column hydro dynamics better fits the adsorption system. Therefore in the present investigation it was summarized that large flow rates and smaller bed heights rendered the minimum possible resistance for the transfer of metal ions from liquid phase to packed bed.It was concluded that based on the analysis of data obtained in continuous flow operation from breakthrough curves it was concluded that the mixed adsorbent can be treated as the better adsorbent for the removal of copper and cadmium.

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