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Removal of Copper and Cadmium from industrial effluents using the mixed adsorbent in the Continuous flow operations

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ABSTRACT

Mixed adsorbent prepared by blending Activated charcoal and bone charcoal in 1: 1 ratio was used to remove the Cu (II) and Cd (II) from the industrial effluents in the continuous flow operation and these investigations are reported in this paper. The effect of volumetric flow rate, mass of the adsorbent was studied for both the metals. The column studies were carried out at room temperature with mass of the adsorbent varying from 50, 100 and 150 g and volumetric flow rate varying from 10, 20 and 30ml/min. The potential capacity of the mixed adsorbent as a low cost material for the removal of Cu (II) and Cd (II) from the synthetic metal ion solution or industrial effluents has been studied. The influence of parameters like flow rate, bed height on breakthrough curves and adsorption performance of the mixed adsorbent were reported in terms of adsorption capacity. The data obtained from these experiments were fitted to dynamic adsorption models such as Thomas model, Yoon-Nelson model which gave a better fit to the experimental data under various conditions. The highest uptake capacity (54.31 mg/g for Cu and 30.31 mg/g for Cd) was obtained at bed height of 12cm at an inlet concentration of 100mg/l with a flow rate of 10 ml/min.

Key words: Continuous flow operation, weight of the adsorbent, volumetric flow rate, Thomas model, Yoon-Nelson model, Breakthrough curves

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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 (Ahalya N, Ramachandra T.V et.al 2003), 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].

In this paper a systematic and detailed study have been carried out to find the adsorption capacities of Cd (II) and Cu (II) as mixed adsorbent prepared by mixing Activated charcoal and Bone Charcoal (1:1 ratio) in Continuous flow operation and these results are presented. Also dynamic models were studied i.e. (Yoon-Nelson model and Thomas model) to fit the experimental data and to plot the break through curves

EXPERIMENTAL SECTION

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 (4cm internal diameter and 100cm 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 (100mg/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).

2.1.1.1 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 12cm, 24cm, 36cm and the flow rates varying from 10, 20, 30 ml/min with an initial concentration of 100ppm. The main design of the column involves the study of break through curves experimentally and to compare with the theoretical models such as Yoon- Nelson model, Thomas model.

Parameters & Dimensions of the packed bed column

Weight of the mixed adsorbent added 50g, 100g, and 150g respectively (for 12cm -25g each; for 24cm -50g each; for 36cm -75g 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 = 40Watts.
Initial Metal Con of the metal ions Cu and Cd (C_o) = 100ppm
Effect of volumetric flow rate -10, 20, 30 ml/min
Effect of Weight of the adsorbent (bed height) -12cm, 24cm, 36cm

Fig 1 Experimental setup of Continuous flow column

2.1.1.2 Analysis of the column data

The analysis and behavior of the Continuous column flow operation can be determined by using the time taken to reach breakthrough and the shape of the breakthrough curve. The breakthrough curves show the loading behavior of the metal ions in a Continuous column [9] and are normally expressed in terms of the normalized concentration defined as the ratio of the outlet effluent concentration (C_t) to the inlet concentration (C_o) as a function of time (in minutes). The analysis of the column is expressed in terms of various theoretical breakthrough models such as Thomas model, Yoon-Nelson model to predict the nature and behavior of the adsorption process.

2.1.1.3 Data Modeling

Thomas model

Thomas (Thomas, 1994) developed a model for adsorption processes in which external and internal diffusion limitations are not present. The linearized form of the Thomas model can be expressed below as (Ahmad and Hameed, 2010) [14]

$$\ln\left(\frac{c_0}{c_t}-1\right)=\frac{k_{Th}q_o m}{Q}-\frac{k_{Th}C_o t}{m} \quad (1)$$

Where k_{Th} is the Thomas model constant (ml/min. mg), q_o is the equilibrium uptake capacity of the Cu and Cd (mg/g), C_o is the inlet concentration (100mg/l). C_t is the effluent metal ion concentration at time t (mg/l), m is the mass of the adsorbent (g). Q is the inlet flow rate (ml/min) and t is the flow time (min). The value of $\left(\frac{C_O}{C_t}\right)$ is the ratio of inlet to outlet metal ion concentrations. A linear plot of $\ln\left(\frac{C_O}{C_t}-1\right)$ against time (t) was plotted to determine the values of q_o and K_{Th} from the intercept and slope respectively.

The Yoon-Nelson model

Yoon and Nelson (Yoon and Nelson, 1984) [15] developed a model to describe the adsorption behavior in the Continuous column flow operations. The linearized form of the Yoon-Nelson model is given by

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = k_{YN}t - \tau k_{YN} \quad (2)$$

Where k_{YN} is the rate velocity constant (L/ min) and τ is the time (min) required for 50% adsorbate breakthrough. A linear plot of $\ln\left(\frac{C_t}{C_o - C_t}\right)$ against sampling time (t) was used to determine the values of K_{YN} and τ from the slope and intercept of the plot [16]. The calculated and τ value obtained from the model is compared from the experiment.

RESULTS AND DISCUSSION

3.1.1 Continuous flow operation

In the continuous flow operation, the results discuss the effect of adsorbent dosage on break through curves for different flow rates at a constant Initial Metal Ion concentration (IMC) C_o. Further it also discusses about the kinetic models in the continuous flow operation which includes Thomas and Yoon-Nelson models.

3.1.2 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 [10, 11]. 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).

3.1.3 Effect of adsorbent dosage

The adsorption of metal ion in the packed bed column is directly proportionally to the quantity of adsorbent in the column. The blended adsorbent (1:1 ratio) of 50 g, 100 g, and 150 g are added from the top of the column. The adsorption breakthrough curves are obtained by changing the bed weight at various stream rates (flow rates) of 10 ml/min, 20 ml/min, 30 ml/min. Faster breakthrough curves were observed for a bed weight of 50g, while the slowest breakthrough bend was seen at a bed weight of 150 g. Higher the absorbent weight, more the active sites that are accessible for the metal particles to attach and diffuse deep on to the pores of the adsorbents and on to the surface [12] which leads to the achievement of higher bed capacity. Furthermore an increment in the bed weight brought about more contact time that was being accessible for the metal particle to interact and bind with the adsorbent [13]. This phenomenon has permitted the metal particles to diffuse deeper into the mixed adsorbent. Subsequently the percentage of metal ion removal increased when the bed weight was increased.

3.1.4Effect of volumetric flow rate

The effect of flow rate on the metal ions by the mixed adsorbent was investigated by varying the flow rate of the metal ion solution at different flow rates from 10, 20 and 30 ml/min while maintaining the initial metal ion concentration at 100 mg/l and bed weights at 50 g, 100 g, and 150 g respectively. A plot of metal ion concentration ratio on y-axis vs effluent outlet time on x-axis at different flow rates was plotted. The quicker breakthrough was observed for the lowest flow rate of 10 ml/min. When the inlet flow rate was increased from 10 ml/min to 30 ml/min, the bed capacity decreased from 30.31 to 7.02 mg/g for cadmium and 54.31 to 9 mg/g for copper as shown in the Table 1 and 2 respectively.

At lower flow rates of metal ion solution, the contact time between the metal ions and adsorbent was more [13] which results in a slower breakthrough curve. Conversely at the higher flow rates the metal ion solution will leave the bed before its attainment of equilibrium. This will result in reduced amount of metal ion concentration being adsorbed from the effluent. Biosorption of 2, 4-dichlorophenol in a fixed bed [17] exhibited a similar trend as observed in the present study. The breakthrough curves for Cd (II) and Cu (II) were plotted (as shown in the Fig 2 to 7) which indicates that the faster break through are obtained for cadmium when compared to copper. Due to higher covalent index of Cd (2.71) than Cu (2.61) and low ionization potential of Cd (16.91) when compared to copper (20.3), this type of trend was observed in this study. It was also reported that higher the covalent index, better the adsorption of metal ions on the surface of R. Arrihuzus and S. Cervisiae [18-19]. The saturation time for Cd (II) at 50 g with different flow rates of 10 ml/min, 20ml/min and 30 ml/min were 180 min, 120 min, and 80 min respectively. The saturation time for Cd (II) at 100 g with different flow rates were 320 min, 220 min and 150 min respectively. Similarly the saturation time for Cd (II) at 150 g with different flow rates were 450 min, 320 min, 290 min, respectively were observed from this experimental study.

The saturation time for Cu (II) at 50 g with different flow rates of 10 ml/min, 20ml/min and 30 ml/min were 400 min, 270 min and 200 min respectively. The saturation time for Cu (II) at 100 g with different flow rates were 450 min, 370 min and 270 min respectively. Similarly the saturation time for Cu (II) at 150 g with different flow rates were 600 min, 490 min and 350 min respectively were observed in this experimental study. In the continuous column experiments, the breakthrough point shifted towards right when the adsorbent dosage was increased from 50 g to 150 g at a fixed initial metal ion concentration of 100 ppm.

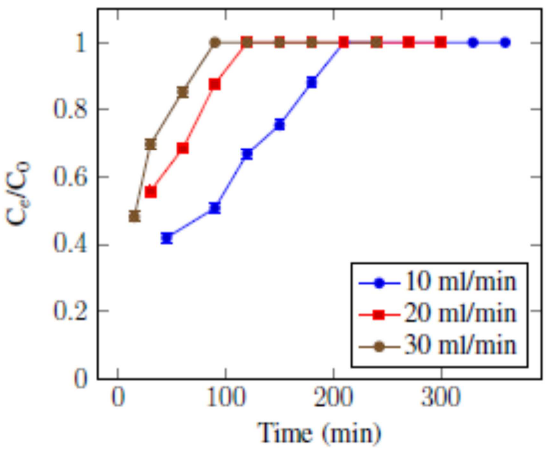

Figure 2: Breakthrough curves for Cadmium at 50 g bed weight, IMC =100 ppm at different flow rates of 10, 20 and 30 ml/min

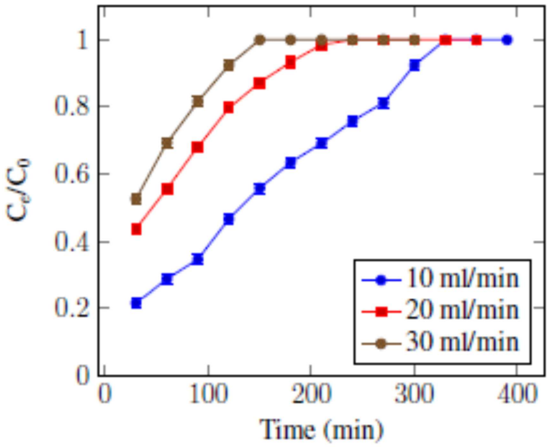

Figure 3: Breakthrough curves for Cadmium at 100 g bed weight, IMC =100 ppm at different flow rates of 10, 20 and 30 ml/min

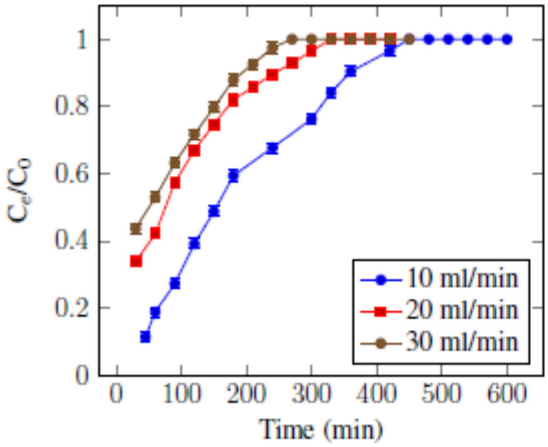

Figure 4: Breakthrough curves for Cadmium at 150 g bed weight, IMC =100 ppm at different flow rates of 10, 20 and 30 ml/min

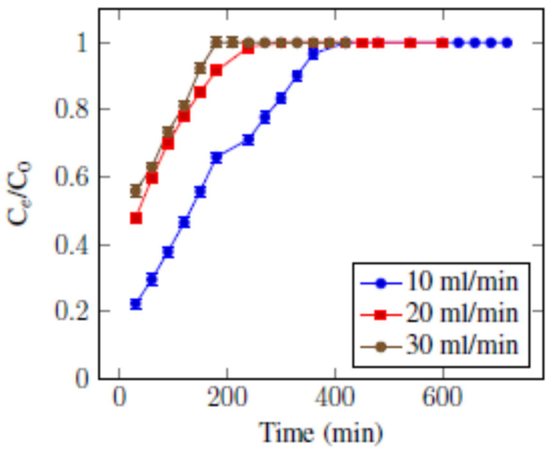

Figure 5: Breakthrough curves for Copper at 50 g bed weight, IMC =100 ppm at different flow rates of 10, 20 and 30 ml/min

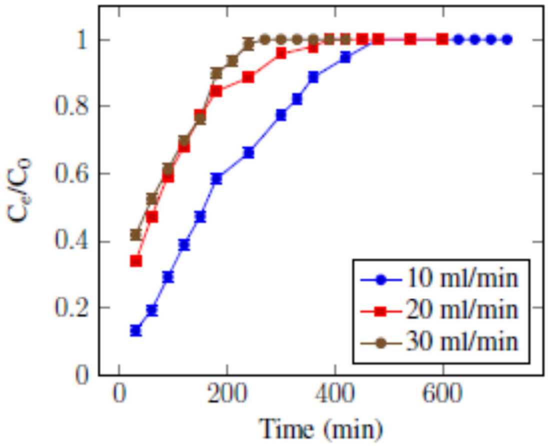

Figure 6: Breakthrough curves for Copper at 100 g bed weight, IMC =100 ppm at different flow rates of 10, 20 and 30 ml/min

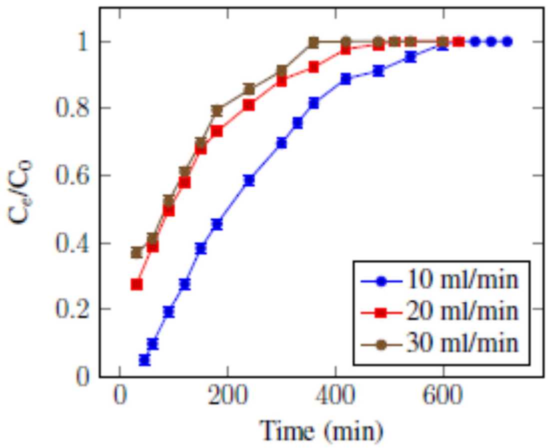

Figure 7: Breakthrough curves for Copper at 150 g bed weight, IMC =100 ppm at different flow rates of 10, 20 and 30 ml/min

Table 1: Thomas model parameters for Cadmium (II)

Column Parameters	Thomas rate constant (K_{Th})	Adsorption Capacity (q_o)	R^2	Model equation
10 ml/min, 50g	0.00855	30.31	0.953	y = -0.017x+1.296
20 ml/min, 50g	0.0144	20.58	0.955	y = -0.029x+0.743
30 ml/min, 50g	0.0198	16.39	0.967	y = -0.04x+0.54
10 ml/min, 100g	0.0127	13.5	0.976	y = -0.0127x+1.715
20 ml/min, 100g	0.0231	10.54	0.953	y = -0.023x+1.217
30 ml/min, 100g	0.0262	8.42	0.991	y = -0.026x+0.736
10 ml/min, 150g	0.0186	7.81	0.973	y = -0.017x+1.296
20 ml/min, 150g	0.02	7.66	0.992	y = -0.014x+1.053
30 ml/min, 150g	0.026	7.02	0.967	y = -0.0175x+1.003

Table 2: Thomas model parameters for Copper (II)

Column Parameters	Thomas rate constant (K_{Th})	Adsorption Capacity (q_o)	R^2	Model equation
10 ml/min, 50g	0.006	54.31	0.954	y = -0.012x+1.63
20 ml/min, 50g	0.009	37.22	0.96	y = -0.02x+0.9352
30 ml/min, 50g	0.0105	32.18	0.946	y = -0.018x+0.4827
10 ml/min, 100g	0.0112	17.56	0.986	y = -0.0112x+1.9676
20 ml/min, 100g	0.0132	13.28	0.99	y = -0.0132x+0.8765
30 ml/min, 100g	0.07	10.87	0.93	y = -0.0202x+1.91
10 ml/min, 150g	0.01725	15.29	0.963	y = -0.0115x+2.64
20 ml/min, 150g	0.0174	12.21	0.981	y = -0.0116x+1.177
30 ml/min, 150g	0.02685	9	0.83	y = -0.0179x+1.64

4. Modelling of Kinetic studies for Continuous Operation

An adsorption model was used to predict the fixed-bed dynamics including external film diffusion and intra particle mass transport, the former resulting the limiting step to overall mass transport in the investigated experimental conditions. The main fluid dynamic and physical parameters, such as flow rate and metal ion concentration were investigated, in order to determine their effect on the overall adsorption rate. This information is commonly considered as fundamental for a proper device scale-up, for a cost-effective adsorption column design and for a general process optimization. Finally, a thorough modelling analysis of the fixed-bed column was carried out as a support for the design of adsorption units for copper and cadmium removal from polluted/industrial waste water. The kinetic studies in the continuous column operation were used to describe the sorption isotherms of single-solute systems in the form of linear break through models such as Thomas model and Yoon-Nelson model which explains the mechanism of adsorption.

4.1 Thomas model

Thomas developed a model for adsorption processes in which external and internal diffusion limitations are not present [14]. A linear graph of $\ln[C_o/C_t - 1]$ against time (t) was plotted to determine the values of q_o and k_{Th} from the intercept and slope respectively. It was concluded for cadmium metal, at a constant bed weight of 50 g and at different flow rates the Thomas rate constant values k_{Th} increased from 0.00855 to 0.0198 and the adsorption capacities decreased from 30.31 to 16.39 mg/g. Similarly at 100 g and 150 g with different flow rates the same trend has been observed and the numerical values are shown in Table 1 for Cadmium. Moreover at all the flow rates and bed weights the Correlation or Regression coefficient R^2 values obtained are in the range of 0.95 to 0.99 that further predicts the suitability / best fit of the Thomas model for the adsorption system of Cadmium. Similarly, it was concluded for copper metal that at a constant bed weight of 50 g and at different flow rates the Thomas rate constant values k_{Th} increased from 0.006 to 0.0105 and the adsorption capacities decreased from 54.31 to 32.18 mg/g. Similarly at 100 g and 150 g with different flow rates the same trend has been observed and the numerical values are shown in the Table 2 for Copper. Moreover at all the flow rates and bed weights the Correlation or Regression coefficient R^2 values obtained are in the range of 0.95 to 0.9 except for 30 ml/min and 150 g. It clearly indicates from Table 2 that the Thomas model gives a best fit for the adsorption system of Cu (II). The Thomas model equations for Cu (II) at 100 g and Cd (II) at 150 g bed weight along with R^2 are shown in fig 8 and 9 respectively.

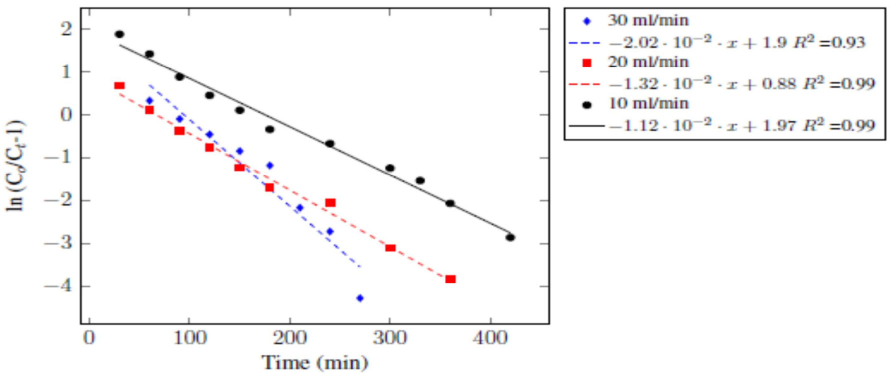

Figure 8: Thomas model for Cu (II) at 100 g bed weight and at different flow rates

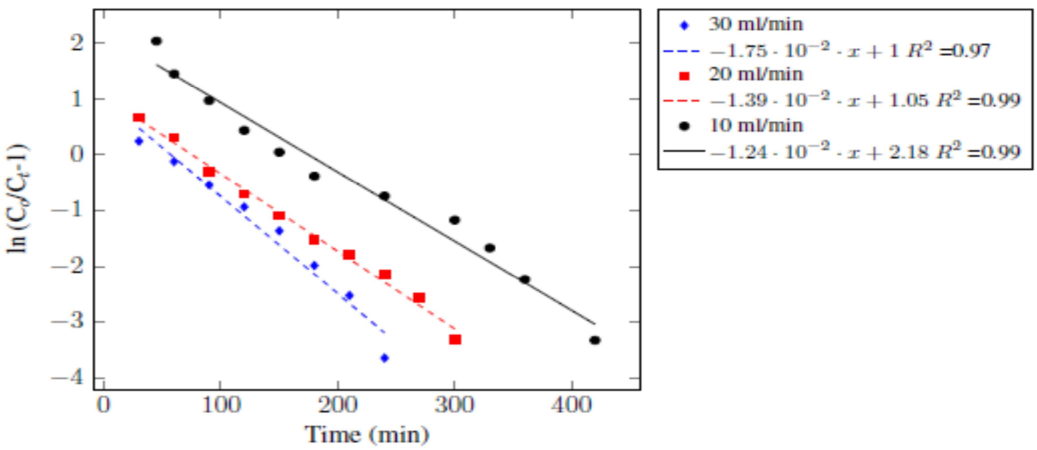

Figure 9: Thomas model for Cd (II) at 150 g bed weight and at different flow rates

4.2 Yoon-Nelson model

This model is mathematically equivalent to the Thomas model, and it has also been applied to a range of concentrations in the effluent between the breakthrough and saturation time of the column [15]. This model is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and probability of adsorbate breakthrough on the adsorbent [16]. Yoon and Nelson built up a model to explain the adsorption phenomena in the Continuous column flow (stream) operation.

A linear graph of ln ($C_t/(C_o$- C_t)) against effluent collection time or reaction time t was used to determine the values of K_{YN} and and τ from the slope and intercept of the plot respectively.

The determination of mathematical equation depends on the definition that 50 % breakthrough happens at t = τ . In this way, the sorption bed was ought to be totally soaked (saturated) at t = τ. Owing to the symmetrical nature of the breakthrough curves due to the Yoon-Nelson model, the measure of metal being sorbed in the fixed bed is half of the aggregate (total) amount of metal ion entering the sorption bed inside 2τ period. This model depends on the hypothesis that the rate of decrease in the probability of adsorption for every adsorbate particle is relative to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent [14]. Several authors have used Yoon and Nelson model in the study of column adsorption kinetics and are cited in the literature [20, 21-22].

Yoon - Nelson model was also applied to the column data obtained from metal ion adsorption by the mixed adsorbent in the continuous flow operation. A plot of ln ($C_t/(C_o$-C_t)) on x-axis time (min) on y-axis gives a straight line with slope of K_{YN}, and intercept of τ K_{YN}. The values of K_{YN}, τ and adsorption capacity q_o are calculated and shown in table 3 and 4 for Cd (II) and Cu (II) respectively.The Yoon-Nelson model equations for Cu (II) at 100 g and Cd (II) at 150 g bed weight along with R^2values are shown in fig 10 and 11 respectively.

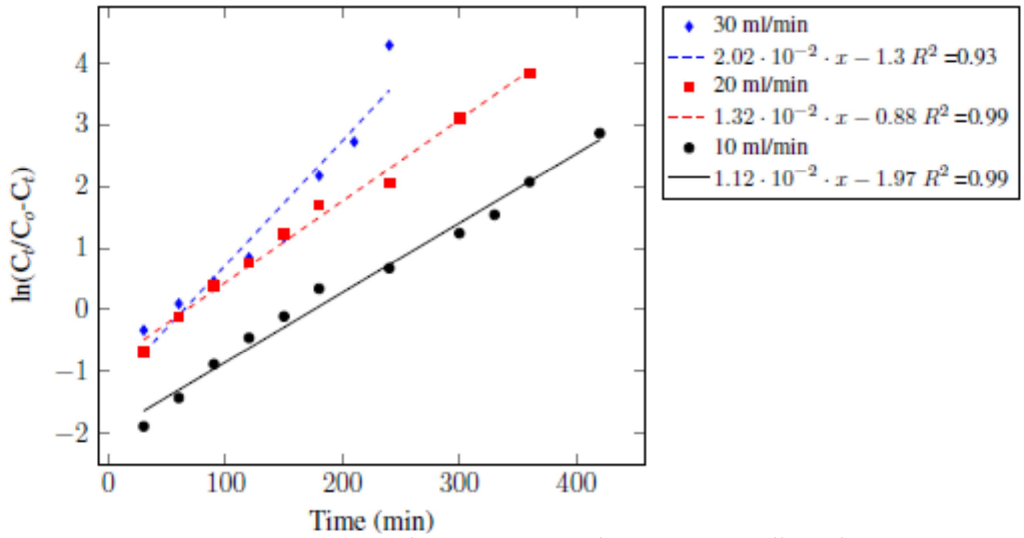

Figure 10: Yoon- Nelson model for Cu (II) at 100 g of bed weight and different flowrates

The results proved that the Yoon-Nelson rate constant, K_{YN} increased with the increment of flow rate and bed weight at a constant IMC (Initial Metal ion Concentration) of 100 ppm. Also the adsorption capacity q_o decreased with increase in bed weight and also decreased with increase in flow rate from 10 ml/min to 30 ml/min at a constant Initial metal ion concentration. The time required for 50% breakthrough (τ) decreased with the increase in flow rate at fixed initial metal ion concentration and τ also increased with the increase in the bed weight (adsorbent packed in g). High values of correlation coefficients (R^2) indicate that Yoon–Nelson model fitted equally well with the Thomas model for the obtained experimental data. This is in good agreement with the experimental results obtained from [21] and [23]. The results indicate that the K_{YN} values increased from 0.012 to 0.020 l/min and τ values decreased from 135.78 to 26.67 min when the flow rate increased from 10 ml/min to 30 ml/min at 50 g of the adsorbent dosage for Cu (II) and Cd (II) as shown in Table 3 and 4 respectively. The linear regression coefficient (R^2) was greater than 0.95 at different conditions for all the fitted values in this model which indicates that it can be utilized to explain the overall kinetics in the column studies for Cu (II) and Cd (II) adsorption. It shows that the Yoon-Nelson model is apt to describe the dynamics of the adsorption in the column. Additionally, these results indicate that the rate of decrease in the adsorption probability of metal ions onto mixed adsorbent is directly proportional to the metal ion adsorption and breakthrough on the mixed adsorbent. These results are in good agreement with the results obtained from literature [24].

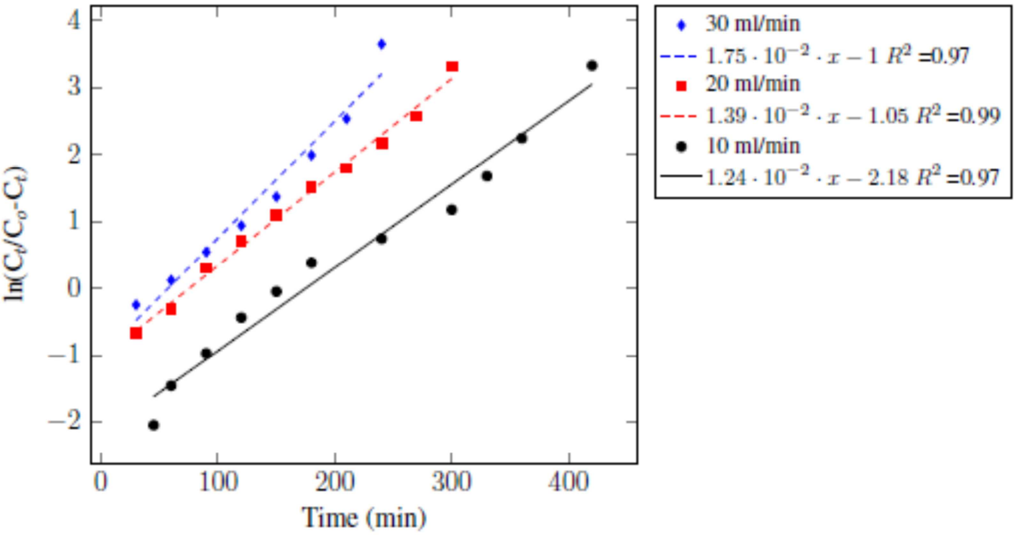

Figure 11: Yoon- Nelson model for Cd (II) at 150 g of bed weight and different flow rates

Table 3 Yoon-Nelson model parameters for Cd (II) at different flow rates and adsorbent dosage

Column Parameters	Yoon-Nelson rate constant (K_{YN})	50% break through time (τ)	Regression Coefficient (R^2)	Model equation
10 ml/min, 50g	0.0171	75.78	0.953	y = 0.0171x-1.296
20 ml/min, 50g	0.0289	25.73	0.955	y = 0.029x-0.7437
30 ml/min, 50g	0.0396	13.66	0.967	y = 0.0396x-0.541
10 ml/min, 100g	0.0127	135	0.976	y = 0.0127x-1.7153
20 ml/min, 100g	0.0231	52.7	0.953	y = 0.0231x-1.2174
30 ml/min, 100g	0.0262	28.1	0.991	y = 0.0262x-0.7358
10 ml/min, 150g	0.0124	175.71	0.973	y = 0.0124x-2.179
20 ml/min, 150g	0.0139	75.8	0.9924	y = 0.014x-1.0537
30 ml/min, 150g	0.0175	57.34	0.967	y = 0.0175x-1.0035

Table 4: Yoon-Nelson model parameters for Cu (II)at different flow rates and adsorbent dosage

Column Parameters	Yoon-Nelson rate constant (K_{YN})	50% break through time (τ)	Regression Coefficient (R^2)	Model equation
10 ml/min, 50g	0.012	135.78	0.9542	y = 0.012x-1.6924
20 ml/min, 50g	0.0181	46.76	0.96	y = 0.0201x-0.9352
30 ml/min, 50g	0.02	26.67	0.946	y = 0.018x-0.4827
10 ml/min, 100g	0.0112	175.67	0.986	y = 0.0112x-1.9676
20 ml/min, 100g	0.0132	66.4	0.991	y = 0.0132x-0.8765
30 ml/min, 100g	0.0202	64.15	0.93	y = 0.0202x-1.296
10 ml/min, 150g	0.0115	229.4	0.9631	y = 0.0115x-2.64
20 ml/min, 150g	0.0116	101.5	0.9813	y = 0.0116x-1.1774
30 ml/min, 150g	0.0179	91.6	0.83	y = 0.018x-1.64

CONCLUSION

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 88-90% of the cadmium ions originally present in the solution were adsorbed onto the mixed adsorbent.

Based on the analysis of data obtained in continuous flow operation from breakthrough curves and kinetic models, it was concluded that the mixed adsorbent can be treated as the better adsorbent for the removal of heavy metal ions. The experimental data obtained proved that the effect of bed weight, flow rate and inlet (initial metal ion) concentration plays a significant role on the removal of Cu (II) and Cd (II).

Major conclusions from continuous flow operation are tabulated in Table 5.

Table 5 Main Outcomes of the Column study- wrt (with respect to) flow rate and adsorbent dosage at fixed Initial metal ion concentration of 100 ppm

Parameter/ Models	**Model Analysis**	**Conclusion**
Effect of bed weight	C_e/C_o was plotted at different bed weights and volumetric flow rates at 10,20, 30 ml/min to find the saturation time for Cadmium and copper respectively	C_e/C_o increases with increase in the bed weight from 50 to 150 g for Cu (II) and Cd (II) and reached the saturation point
Effect of volumetric flow rate	C_e/C_o plotted at different volumetric flow rates while maintain the IMC(Initial Metal ion Concentration) at 100ppm and bed weights at 50, 100, 150 g respectively.	C_e/C_o increases with increase in the volumetric flow rate from 10 to 30 ml/min for Cu (II) and Cd (II) and reached the saturation point
Thomas model	Fitted with higher R^2 values for Cu (II) than Cd (II) at 50, 100g and for 150 g at different flow rates the Cd (II) fitted better than Cu (II)	K_{Th} increased and q_o decreased with the increase of flow rate from 10 ml/min to 30 ml/min at different bed weights for both the metals
Yoon-Nelson model	Fitted the model with higher R^2 values for Cd (II) than Cu (II) at all flow rates and bed weights	τ decreased and K_{YN}increased with the increase of flow rate at various bed weights for both the metals

Abbreviations
Cu (II) – Copper metal ions
Cd (II) – Cadmium metal ions
AC – Activated Charcoal
BC – Bone Charcoal
AIMIL –
N m – Nano meters
AAS – Atomic Absorption Spectrophotometer
IMC – Initial metal ion concentration
MTZ – Mass transfer / exchange zone

Notations / Symbols used
C_t –Outlet effluent concentration (mg/l)
C_o – Inlet effluent concentration (mg/l)
$\frac{C_t}{C_o}$ = ratio of inlet to outlet effluent concentration
K_{Th} – Thomas model constant (ml / min.mg)
q_o – Equilibrium uptake capacity / Adsorption capacity (mg/g)
Q – Inlet effluent flow rate (ml/min)
t – flow time / effluent collection time (min)
m – Mass of the adsorbent (g)
K_{YN}– rate velocity constant (L /min)
τ - Time (min) required for 50% adsorbate breakthrough
t –Sampling time (min) – (used in Yoon Nelson model)
$\frac{C_e}{C_o}$ = loading behavior or concentration ratio of outlet to inlet effluent concentration in terms of time or volume of the effluent
R^2 = Correlation or Regression coefficient

Conflict of Interest
The authors declare that they have no conflict of interest.

REFERENCES

[1] N Ahalya;TV Ramachandra; RD Kanamadi. *Research Journal of Chemistry and Environment;* **2003**,7(4), 71-79.
[2] G Aman;I Tehseen. *Colloids and Surfaces B: Biointerfaces*; **2003**,63 (1), 116-121.
[3] Jiang Yu, Hao Pang, and Bing Liao. *Journal of Hazardous Materials;***2009**,164 (1),1-9.
[4] W Shaobin ; HM Ang; MO Tade. *Chemosphere;***2008**,72 (11), 1621-1635.
[5] RM Bhise. *Research Journal of Recent Sciences;***2012**,1(6), 66-69.
[6] O Innocent;A Emmanuel; A Thomas. *Leonardo Journal of Sciences;***2009**,14 (1), 58-65.
[7] S Ong; C Seng; P Lim. *Electronic* Journal *of Environmental, Agricultural and Food Chemistry*; **2007**.6 (2), 1764-1774.
[8] A Bhattacharya;R Venkobachar . *Journal of Environmental Engineering ;***1984**,110 (1); 110–122.
[9] MT Uddin; M Rukanuzzaman; MMRKhan; MA Islam. *Journal of Environmental Management;* **2009**, 90(11), 3443-3450.
[10] A Erto; RAndreozzi; A Lancia;D Musmarra. *Journal of Applied Surface Science*;**2010**, 256 (3), 5237–5242.
[11] V Leone; S Canzano;P Iovino; S Capasso. *Journal of Porous Materials*; **2012**,19 (4), 449–453.
[12] I Semra; N Macit; K Serpil; O Huseyin. *Turkish Electronic Journal of Biotechnology;***2004**, 2 (3), 50–57.
[13] K Amela;H Abdeslam;MD Kerroum. *Energy Procedia*; **2012**,19 (5), 286–295.
[14] Nasehir Khan, E Ismail; Muhamad Faizal Pakir; A Olugbenga;M Solomon; A Mohd Azmier Bello. *International Journal of Engineering and Technology*; **2011**,11(4), 248–252.

[15] MA Martin-Lara; ILR Rico; ILR Vicente; IDA Vicente; GB Garcia;MC Dettoces. *Desalination*;**2008**,256 (2), 1-3.
[16] R Han; Y Wang; X Zhao; Y Wang; F Xie; J Cheng; M Tang. *Desalination*;**2009**,245(2), 284–297.
[17] J Wu; HQ Yu. *Chemical Engineering Journal*;**2008**,138 (4), 128–135.
[18] JM Tobin; JM Ba. *Journal of Enzyme Microbe Technology*;**1994**,17(1), 791–796.
[19] C Chen, J Wang. *Chemosphere*;**2007**,69 (4), 1610–1616.
[20] JT Nwabanne; PK Igbokwe. *International Journal of Applied Science and Technology;***2012**,2 (4), 106–115.
[21] WT Tsai; CY Chang; CY Ho; LY Chen. *Journal of Colloid and Interface Science*;**1999**, 214 (5), 455–458.
[22] P Sivakumar; PN Palanisamy. *International Journal of Chemical Technology and Research* **2009**;1(3), 502–510.
[23] AA Ahmad; BH Hameed; N Aziz. *Journal of Hazardous Materials*;**2006**,94 (2),1–10.
[24] KY Foo, BHA Hameed. *Journal of Hazardous Materials*;**2009**,171 (2), 6-14.