

# **Removal of chromium and Iron using mixed adsorbent for synthetic and industrial samples in a continuous column reactor**

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## **Abstract**

*The results of the experiments showed that bed weight, flow rate, and initial metal ion concentration all play a role in the removal of Cr (III) and Fe (II). The optimized break through curve was obtained at 36cm bed height and 10ml/min for chromium where 97.5 to 100% removal was observed at a saturation time of 500-600 min. With the increase in bed height from 12cm to 36cm, both the breakthrough and saturation times for Cr (III) increased. The break through time at 12cm, 24cm, 36cm and 10ml/min for Cr (III) were 70 min, 105 min, and 35 min respectively. The saturation time for Cr (III) at 12cm, 24cm, 36cm and 10ml/min were 460 min, 490 min, and 500 min respectively. Similarly, the break through time for Fe (II) at 12cm, 24cm, 36cm and 10ml/min were 70 min, 80 min, and 100 min respectively. At 12cm, 24cm, 36cm, and 10ml/min, the saturation time for Fe (III) was 340 minutes, 360 minutes, and 430 minutes, respectively. Overall in the column performance comparison between synthetic solution and industrial effluents for chromium, synthetic solution performance was more superior at fixed volumetric flow rates of 10 ml/min and bed heights ranging from 12 cm to 36 cm. But the reverse trend was observed in case of fixed bed heights of 36 cm (150 g) and variation of volumetric flow rates from 10ml/min to 30ml/min which indicates that industrial effluent performance was superior when compared to synthetic solution for heavy metal removal.*

**Key words:** *Bed weight, Volumetric Flow rate, Initial Metal ion Concentration, Break through curve, Saturation time, Break through time, Synthetic solution, Industrial effluents*

## 1. Introduction

Heavy metal ion contamination of surface waters has become a serious ecological and health issue due to their toxic effect even at low concentrations. Heavy metals are a particular source of concern because

They are non-biodegradable and thus long-lasting. Heavy metal ions such as cobalt, copper, chromium, nickel, palladium, lead, and zinc have been found in mining waste streams [1], tanneries [2], electronics [3], electroplating, batteries [4] and petrochemicals [5] industries has major effects on the human and aquatic life [6].

Water pollution is still a major issue in the environment as a result 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 their presence in water streams causes bioaccumulation in living organisms, resulting in animal health problems, plants and human life damage [7]. Industrial effluents containing enormous quantities of inorganic and organic chemical wastes, which are steadily become more difficult to treat by ongoing conventional methods.

For the treatment of organic-contaminated wastewater, conventional treatment technologies such as chemical precipitation, ion exchange, electrodialysis, membrane separations, reverse osmosis, and solvent extraction and adsorption have been considered. Adsorption was discovered to be the most effective method among them [8]. Adsorption has been found to be superior to all other treatment methods due to its simplicity of design, ease of operation, and ability to efficiently adsorb a wide range of different types of adsorbate concentrations. Commercial activated carbon is widely regarded as the most effective material for reducing 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 adsorbate particle travels from the fluid segment to the boundary, where it remains for a phase interval. In a rescindable method, particles return to the segment from which they came or reversibly cross into another segment while 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 breakthrough curve concept was used to describe the performance of a fixed-bed column. The time for breakthrough appearance and the shape of the breakthrough curves are critical

characteristics for determining an adsorption column's operation and dynamic response. In most cases, the loading behaviour of a metal ion to be adsorbed from solution in a fixed-bed is expressed in terms.  $C_e/C_o$  as a function of time or effluent volume for a given bed weight, yielding a breakthrough curve

In any case, the efficiency of an adsorption treatment is primarily determined by the thermodynamic aspects of solute-solvent-sorbent interactions as well as transport phenomena involving diffusive-convective transport within porous media [11, 12].

In a fixed-bed device, contaminated water is introduced from the top of the column into a clean bed of mixed adsorbent, and pollutant removal occurs in a narrow band at the top of the column known as the mass transfer / exchange zone (MTZ). As the operation progresses, the upper layers of blended adsorbent become saturated (soaked) with solute, and the adsorption zone moves downward until it reaches the bottom of the column. Under these conditions, the concentration of solutes in the effluent begins to rise. The extent of the MTZ is primarily determined by the liquid-solid relative velocity and the adsorbent properties (particle diameter, micro porous structure).

The greater the MTZ extent, the less efficient the use of the adsorbing bed. Experiment results showed that increasing the initial concentration and the liquid flow rate results in a shorter breakpoint time; additionally, the breakthrough curves become steeper as a result of higher velocity, which improves external mass transport. Break through curves are plots that show a relationship between  $\ln(C_e/C_o)$  vs reaction time in terms of various linear models (with different parameters) and predict the nature of the adsorbent-adsorbate system. They are affected by the volumetric flow rate, the weight of the adsorbent packed at various bed weights, and the initial metal ion concentration of the metal ion solution. The concentration ratio profile is obtained by studying the 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 for the removal of Fe (II) and Cr (III) using mixed adsorbent prepared by mixing activated charcoal and bone Charcoal in continuous flow studies, (1:1 ratio) is used, and the results are presented in the form of a break through curve.

## 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 reagents and buffer solutions used in the study were of Analytical grade.

### 2.1 Methods

Absorption of Atoms A spectrophotometer (Thermo Scientific ICE 3000 series) was used to examine Cr (III) and Fe (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 mixed adsorbent's average particle diameter was determined to be 572.2 nm (Nano meters).

### 2.1.2 Column Studies

Experiments with continuous flow operation were carried out in a transparent cylindrical plastic column (4cm internal diameter and 100 cm height). A stainless sieve with a mesh size of 20 was attached to the bottom of the column. To achieve the desired bed height, a known quantity of the adsorbent in the ratio of 1:1 (mixed adsorbent) was added to the column (12cm, 24cm, 36cm). Cr (III) and Fe (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 column's exit at various bed heights and time intervals until equilibrium was reached and analyzed using an Atomic Absorption Spectrophotometer (AAS). The diagram below depicts the experimental setup of the Packed bed column, as shown in Figure 1. The experimental setup consists of two parts: (1) a reservoir tank and (2) a peristaltic pump to transport the water from Reservoir tank (3) Packed bed filled with 50% each mixture of Activated Charcoal and Bone charcoal

### 2.2 Parameters & Dimensions of the packed bed column

Weight of mixed adsorbent added 50g, 100g, and 150g (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 to send the effluent into the column consumes 40 Watts.

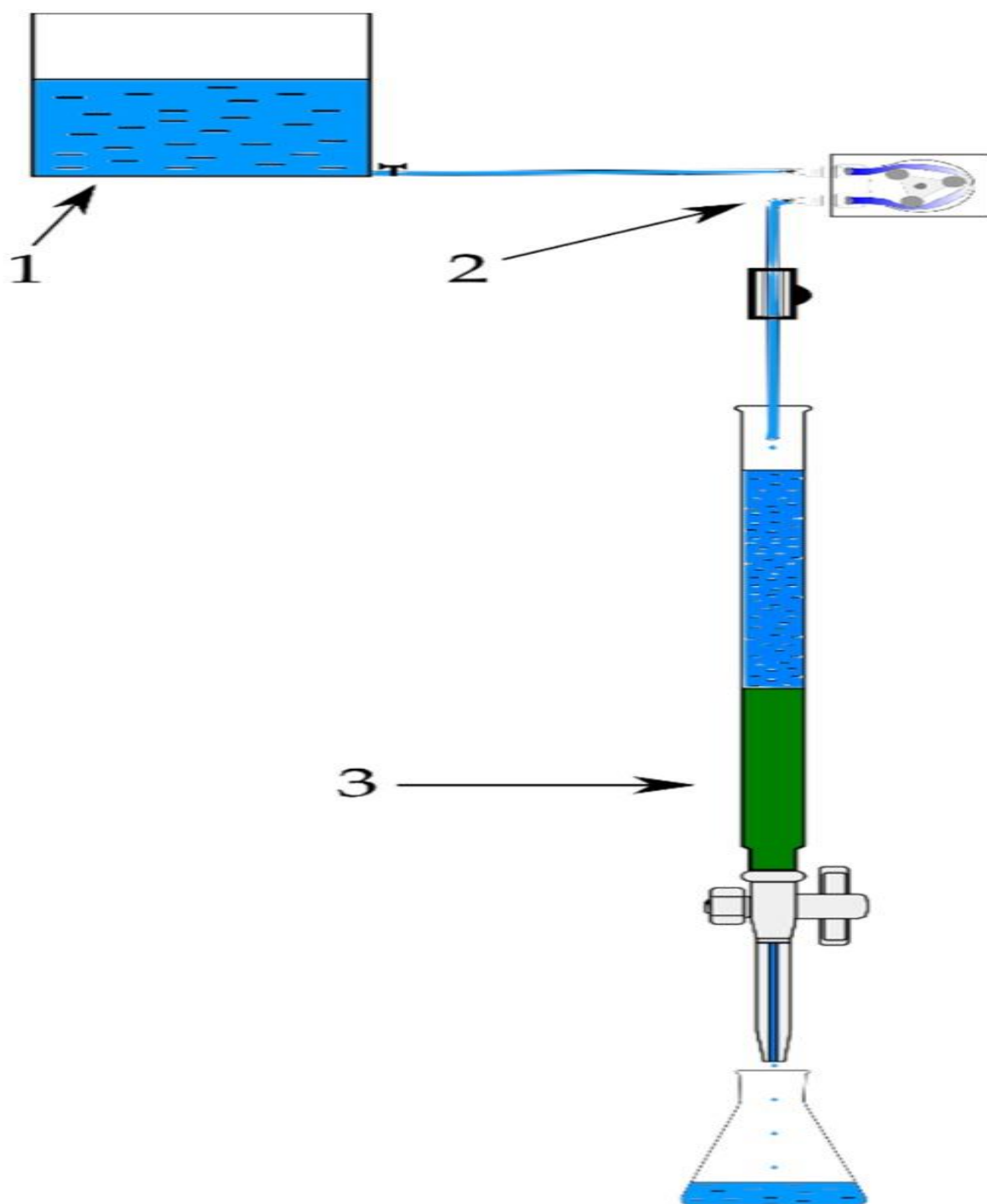
Initial Metal Con of the metal ions Cr and Fe ( $C_0$ ) = 100 ppm

Volumetric flow rates of -10, 20, and 30 ml/min have an effect.

Effect of adsorbent weight (bed height) -12cm, 24cm, 36cm

### 2.3 The investigation of bed heights (adsorbent weight) and volumetric flow rate

The packed bed column design was investigated at bed heights of 12cm, 24cm, and 36cm, as well as flow rates ranging from 10, 20, and 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.



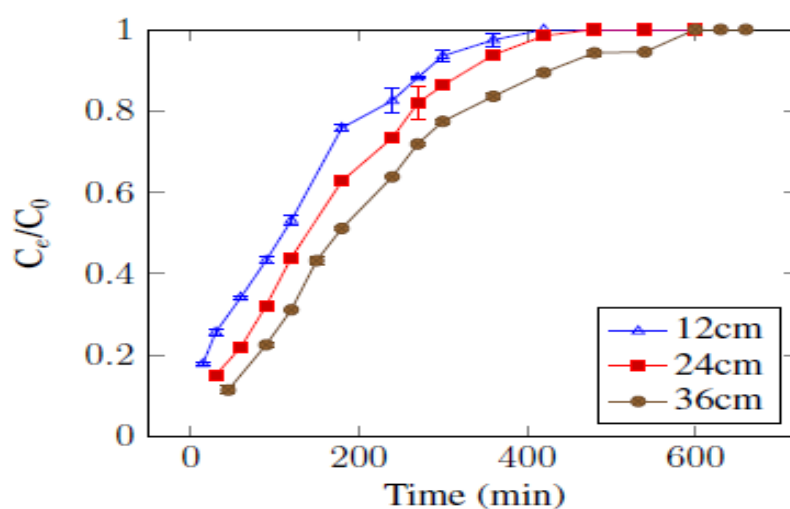
**Fig 1 Laboratory Experimental setup of Continuous flow column**

### 3. Results & Discussion

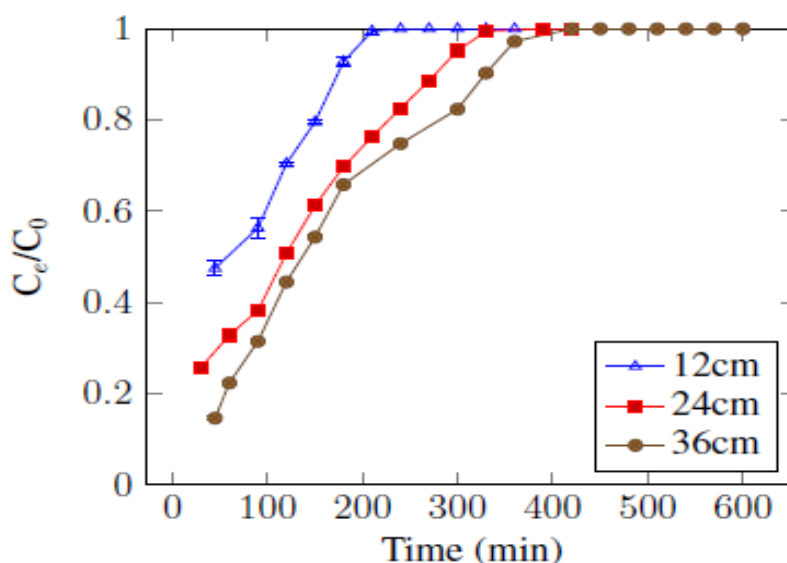
Continuous column study experiments were conducted for both chromium and Iron in packed bed column for the parameters such as effect of bed height (12, 24, 36cm) at fixed volumetric flow rate of 10 ml/min, and effect of volumetric flow rate (10, 20, 30 ml/min) at fixed bed height of 36cm are carried out and the results were compared with the synthetic solution data in terms of % removal, breakthrough time and saturation time.

### 3.1 Effect of bed height and adsorbent dosage on the removal of Cr (III) and Fe (II) from industrial effluent

The adsorption of metal ions in the packed bed column was found to be directly proportional to the amount of adsorbent in the column. The blended adsorbent (1:1 ratio) of 50 g, 100 g, and 150 g are taken in the column and experiments were carried out in order to investigate the parameters and assess the efficiency of the column in the adsorption process. The adsorption breakthrough curves are obtained by varying the bed height between 12, 24, and 36 cm while maintaining a constant volumetric flow rate of 10 ml/min. A bed height of 12 cm resulted in faster breakthrough curves, while a bed height of 36 cm resulted in the slowest breakthrough curve. Higher the adsorbent packed in the column, more the active sites that are accessible for the metal particles to attach and diffuse deep on to the pores as well as on to the surface of the mixed adsorbent [13] which leads to the achievement of higher bed capacity. Further, when the flow rate is less, the metal ion solution has more contact time to run in the column and the increment of bed height brought more active sites that were being in contact with the metal ions to interact and bind with the adsorbent [14]. This phenomenon has permitted the metal particles to diffuse deeper into the active sites of the mixed adsorbent. As a result, increasing the bed height increased the percentage of metal ion removal. The breakthrough and saturation times for Cr (III) increased as the bed height increased from 12 cm to 36 cm. The break through time at 12, 24, 36 cm and 10 ml/min for Cr (II) were 70, 105, and 35 min respectively. The saturation time for Cr (II) at 12, 24, 36cm and 10 ml/min were 460, 490, and 500 min respectively. It can be observed from **Figs. 2 and 3** that the optimized break through curve were obtained at 36 cm bed height and 10 ml/min and further predicts that 36 cm bed height was chosen as the optimal value, and subsequent experiments were carried out at 20 ml/min, 30 ml/min, and 36 cm bed height to investigate the effect of volumetric flow rate on Cr(III) and Fe (II) metal ion removal using packed bed column. Similarly, the break through time for Fe (II) at 12, 24, 36cm and 10ml/min were 70, 80, and 100 min respectively. The saturation time for Fe (II) at 12, 24, 36 cm and 10 ml/min were 340, 360, and 430 min, respectively.



**Fig 2 Breakthrough curves for chromium at 10 ml/min flow rate, IMC of 100 ppm at different bed heights of 12, 24 and 36 cm**



**Fig 3 Breakthrough curves for iron at 10 ml/min flow rate, IMC of 100 ppm at different bed heights of 12, 24 and 36 cm**

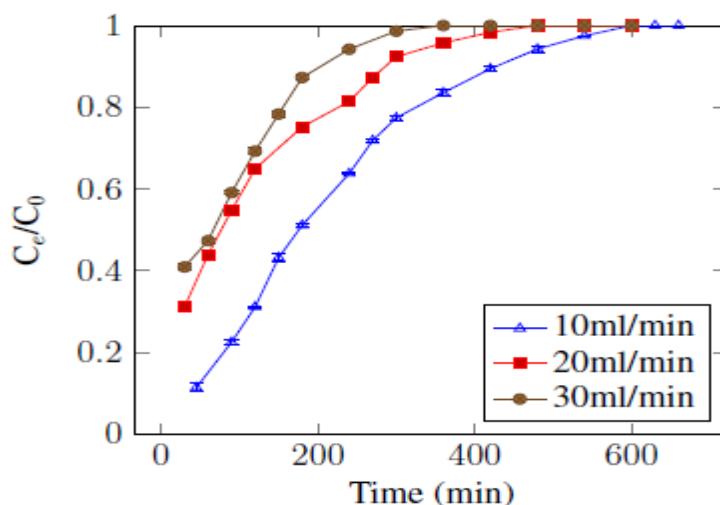
### 3.2 Effect of volumetric flow rate on Cr (III) and Fe (II) removal from industrial effluent

The effect of flow rate on Cr (II) and Fe (II) ions from industrial effluent using the mixed adsorbent was investigated by varying the flow rate of the metal ion solution from 10, 20, and 30 ml/min while maintaining the fixed initial metal ion concentration of 100 mg/l and bed height at 36 cm (150 g). At different flow rates, a graph of metal ion concentration ratio on y-axis vs effluent outlet time / sampling time on x-axis was plotted. Due to less contact time between the metal ion particle and the mixed adsorbent, the highest flow rate of 30 ml/min with a bed height of 36 cm resulted in a faster breakthrough.

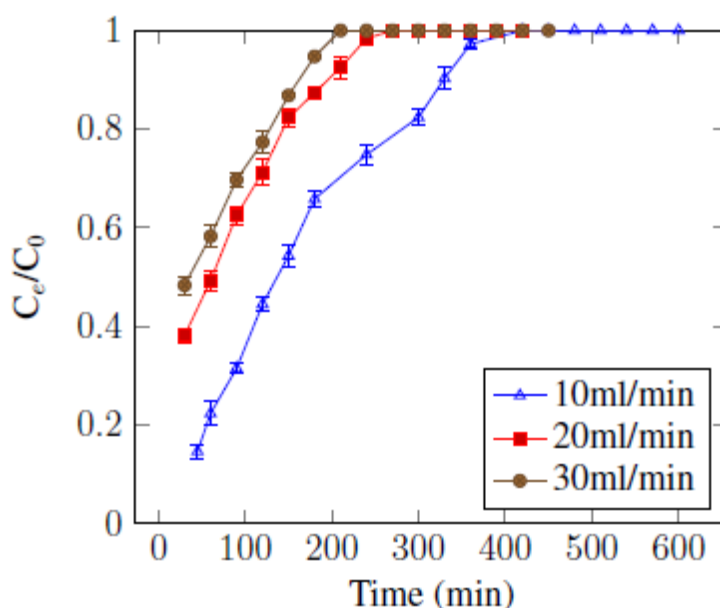
When the volumetric flow rate increased, there was less contact time between the metal ion and the adsorbent, resulting in a decrease in bed capacity. However, at lower flow rates of metal ion solution, the contact time between the metal ions and the adsorbent was longer [14], resulting in a slower breakthrough curve. At higher flow rates, the metal ion solution will leave the bed before reaching equilibrium. As a result, less metal ion concentration will be adsorbed from industrial effluent.

The break through time and saturation time for Cr (III) at 36 cm (150 g) with different flow rates of 10, 20, 30 were 35 and 500 min; 20 and 360 min; 10 and 230 min, respectively were observed in this experimental study. Similarly, the break through time and saturation time for Fe (III) at 36 cm (150 g) with different flow rates of 10, 20, 30 ml/min were 100 and 430 min; 80 and 280 min; 50 and 250 min, respectively were observed. In the continuous column experiments, the breakthrough point shifted towards the right side for both Cr (III) and Fe (II) (II) when the adsorbent dosage was increased from 50 to 150 g with a constant initial metal ion concentration of 100 ppm. It was observed from the **Fig 4 and Fig 5** that the optimized breaks through curves were obtained at 36 cm and 10 ml/min for both Cr (III) and Fe (II). A longer

breakthrough time implies better adsorption capacity which means that it would take a longer time for the adsorbent material to completely get saturated with the adsorbate solution.



**Fig 4: Chromium breakthrough curves at 36cm BH, IMC of 100 ppm, and flow rates of 10ml/min, 20ml/min, and 30ml/min.**



**Fig 5: Breakthrough curves of iron at 36cm BH, IMC of 100 ppm at different flow rates of 10ml/min, 20ml/min, and 30ml/min**

### 3.3 Comparative studies for industrial effluent and synthetic sample in continuous flow study

The results obtained through column studies using industrial and synthetic solutions for copper and cadmium were compared in terms of breakthrough time, saturation time and % removal of metal ions. There was a small significant time difference of break through time (70, 90, 100 min) for synthetic solutions at fixed volumetric flow rates and variation of bed height in comparison with industrial sample having (70, 105, 35 min) for chromium. This large time



difference in industrial effluent was due to the presence of other heavy metal ions like phenol, cresol, heavy metal pollutants other sludge in the industrial effluent so that it has taken more time to reach break through points.

Similarly, the same trend for chromium was observed for saturation time (more time taken in case of industrial effluent) in comparison with synthetic solution and this may be due to the presence of other heavy metals which blocks the adsorbent pores and in turn leads to more saturation time. But in case of different volumetric flow rates and fixed bed heights of (36 cm or 150 g dosage) a huge time difference of 270 min for industrial effluents , 275 min for synthetic effluents) was observed for saturation time as shown in **Table 1 and Table 2.** respectively.

This was due to the increase in dosage from 50 g to 150 g in the column, as there was a greater number of active sites present in the column that are readily available for metal ions to occupy and further leads to saturation delay. But in case of breakthrough time at fixed bed height of 36cm and varying volumetric flow rates there was a difference of 65 min, 60 min, 60 min were observed at 10, 20, 30 ml/min respectively between the industrial and synthetic solutions for chromium removal.

This was due to the increase in volumetric flow rate from 10 to 30 ml/min. More metal ion solution was passed through the column as the flow rate increased, and there was a competitive adsorption of metals ions for the same active sites, and due to the presence of other heavy metals, the pores became blocked quickly, resulting in a difference in breakthrough time and break through achieved late for synthetic solutions.

In comparison with column performance in terms of total % removal at 12 and 24 cm and a fixed vol. flow rate of 10 ml/min, the more % removal was observed in case of synthetic samples having 61.02% ,68.47% than industrial effluents. The less % removal was observed for synthetic sample (96.20 %) at 36 cm bed height (150g) and 10 ml/min when compared to industrial sample having 98.8% as shown in **Table 1 and Table 2.** This difference of 2.6 % removal between the industrial effluent and synthetic sample for copper was due to more adsorbent dosage of 150 g at 36cm bed height. Similarly, at fixed bed height of 36 cm (150 g) and varying volumetric flow rates from 10, 20, 30 ml/min there were a difference of 2.6%, 15.28%, and 16.93 % between industrial effluent and synthetic samples for chromium was observed and this may be due to more dosage of 150 g at 36 cm bed height. Overall in the column performance comparison between synthetic samples and industrial effluents for chromium, synthetic solution performance was more superior at fixed volumetric flow rates of 10 ml/min and bed heights ranging from 12 to 36 cm.

However, a reverse trend was observed for chromium in case of fixed bed heights of 36 cm (150 g) and variation of volumetric flow rates from 10 ml/min to 30 ml/min which indicates that industrial effluent performance was superior as compared to synthetic solution and this may be due to the more adsorbent dosage and influence of synergistic effect in the column. Tables 1 and 2 show the data for industrial effluent and synthetic chromium solution,

respectively. Similarly, for iron there was a significant time difference of breakthrough time (60, 25, 50 min) for synthetic solutions and industrial effluent having (70 min, 80 min, 100 min) at fixed volumetric flow rates and variation of bed height for iron was observed.

The breakthrough time increases for iron -industrial effluent due to the presence of other heavy metals, phenols, cresols, and other sludge that affects the performance of the packed bed column and also gives competitive adsorption effect for iron along with other metals present in the industrial effluent which was sent in the column.

Similarly the same trend was observed for iron in-terms of saturation time in comparison with the synthetic solution and this may be due to presence of other heavy metals that blocks the adsorbent pores and in turn leads to more saturation time at fixed volumetric flow rate of 10 ml/min and different bed heights of 12 and 24 cm. But at 36 cm and 10 ml/min, for the iron removal, the saturation time for industrial effluent decreased (430 min) in comparison with synthetic sample having (460 min) and this may be due to an increase in bed height, which results in increased adsorption capacity (due to adsorbent dose) in the column, as well as due to the presence of synergistic effect of the mixed adsorbent which leads to quick saturation time for industrial effluent.

In case of fixed bed height of 36 cm (150 g) and different volumetric flow rates from 10 to 30 ml/min, the break through time increased from 50 to 100 min at 10 ml/min, 30 to 80 min at 20 ml/min, and the break through time increased from 10 to 50 min at 30 ml/min as shown in **Tables 3 and 4**. This increase in break through time for industrial effluent was due to the presence of other heavy metals and sludge that plays a role of competitive adsorption in the column along with iron [15-17].

Similar to chromium, a reverse trend for iron was observed in-terms of saturation time at fixed bed height of 36 cm and different volumetric flow rates. [18-19]. The saturation time was more for synthetic samples (460, 340 min) when compared to industrial effluents (430, 280 min) and this may be due to the presence of synergistic effect of the mixed adsorbent as well as high amount of dose (150 g) in the column [20-21].

The reverse trend for iron was observed at 30 ml/min and 150 g, where the saturation time was less in case of synthetic sample (220 min) when compared to industrial effluent having (250 min) and this may be due to more volumetric flow rate of (30 ml/min) as well as due to the presence of other heavy metals that blocks the adsorbent particles and further leads to the late arrival of saturation zone as shown in the **Tables 3 and 4**.

In comparison with the column performance of iron in terms of total % removal, at 12, 24, 36 cm and 10 ml/min (fixed volumetric flow rate), the more % removal was observed in case of synthetic samples having 35.7%, 70.03%, 73.63 % in comparison with industrial sample having 29%, 55.69 %, 52.86%, respectively.

The different type of trend for chromium was observed at fixed bed height of 36 cm (150 g) and different volumetric flow rates of 10, 20, and 30 ml/min [22-23]. The more % removal was observed for industrial samples having 96.2%, 72.63%, and 81.77% in comparison with synthetic effluents having 98.8%, 87.91%, and 98.71% which was due to the presence of other heavy metals, sludges apart from competitive adsorption of chromium present in the industrial effluent [24-25]. Overall in comparison with industrial effluents for iron, the synthetic solutions have proved to be more superior in terms of total % removal and better performance was observed with synthetic solutions rather than industrial effluents for iron as shown in **Tables 3 and 4** respectively. For a similar comparison studies with chromium, the industrial effluents proved to be more percentage removal as compared to synthetic solutions [23-25].

**Table 1: Column performance calculations of industrial effluent for chromium removal at different bed heights and volumetric flow rates**

Ads dosage (g)	Bed height (cm)	Vol. flow rates (ml/min)	IMC	Break through time (min)	saturation time (min)	Vol treated at breakthrough point (ml)	Vol treated at saturation point (ml)	$M_{ad}(g)$	$m_{total}(g)$	Total % removal
50	12	10	100	70	460	550	4600	271	460	58.9
100	24	10	100	105	490	1000	4900	284	490	57.96
150	36	10	100	35	500	480	5000	494	500	98.8
150	36	20	100	20	360	640	7200	633	720	87.91
150	36	30	100	10	230	480	6900	681	690	98.7

**Table 2: Column performance calculations of synthetic solution (chromium) removal at different bed heights and volumetric flow rates**

Ads dosage (g)	Bed height (cm)	Volumetric flow rates (ml/min)	IMC	Break through time (min)	saturation time (min)	Vol treated at breakthrough point (ml)	Vol treated at saturation point (ml)	$M_{ad}$	$m_{total}(g)$	Total % removal
50	12	10	100	70	440	550	4400	268.5	440	61.02
100	24	10	90	60	460	750	4600	315	460	68.47
150	36	10	100	65	500	680	5000	481	500	96.2
150	36	20	80	55	380	850	7600	552	760	72.63
150	36	30	70	50	225	1000	6750	604	675	81.77

**Table 3: Column performance calculations of industrial effluent for iron removal at different bed heights and volumetric flow rates**

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 treated at saturation point (ml)	$M_{ad}$	$m_{total}(g)$	Total % removal
50	12	10	100	70	340	530	3400	98.6	340	29
100	24	10	100	80	360	620	3600	200.5	360	55.69
150	36	10	100	100	430	940	4300	227.3	430	52.86
150	36	20	100	80	280	1250	5600	215	560	38.39
150	36	30	100	50	250	950	5000	322.5	500	64.5

**Table 4: Column performance calculations of synthetic solutions for iron removal at different bed heights and volumetric flow rates**

Ads dosage (g)	Bed height (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)	$M_{ad}$	$m_{total}(g)$	Total % removal
50	12	10	100	60	200	520	2000	71.4	200	35.7
100	24	10	100	25	335	330	3350	234.6	335	70.03
150	36	10	100	50	460	620	4600	338.7	460	73.63
150	36	20	100	30	340	870	6800	396.2	680	58.26
150	36	30	100	10	220	950	4400	293.8	440	66.77

#### 4. Conclusions

Based on the analysis of data obtained in continuous flow operation from breakthrough curves and kinetic models. It was concluded that the mixed adsorbent is the better adsorbent for heavy metal ion removal. The experimental results demonstrated that bed weight, flowrate, and initial metal ion concentration all have a significant impact on the removal of Cr (III) and Fe (II).

Overall in comparison with industrial effluents for iron, the synthetic solutions have proved to be more superior in terms of column performance, total % removal and better performance was observed with synthetic solutions than industrial effluents in case of iron and a reverse trend was observed for chromium with high % removal for industrial effluents. In continuous column studies, a longer breakthrough time indicates greater adsorption capacity, implying that the adsorbent

material will take longer to become completely saturated with the adsorbate solution. The adsorbent can be used for a longer period of time before it needs to be replaced or regenerated.

## REFERENCES

- [1] N Ahalya;TV Ramachandra; RD Kanamadi. *Biosorption of Heavy Metals Research Journal of Chemistry and Environment*; 2003,7(4), 71-79.
- [2] G Aman;I Tehseen. *Potato Peels as Solid Waste for Heavy Metal Copper (II) Removal from Waste Water/Industrial Effluent. Colloids and Surfaces B: Biointerfaces*; 2003,63 (1), 116-121.
- [3] Jiang Yu, Hao Pang, and Bing Liao. *Removal of Copper (II) Ions from Aqueous Solution by Modified Bagasse. Journal of Hazardous Materials*; 2009,164 (1),1-9.
- [4] W Shaobin ; HM Ang; MO Tade. *Novel Applications of Red Mud as Coagulant, Adsorbent and Catalyst for Environmentally Benign Processes. Chemosphere*; 2008,72 (11), 1621-1635.
- [5] RM Bhise. *Removal of the colour of the Spent Wash by Activated Charcoal Adsorption and Electro Coagulation. Research Journal of Recent Sciences*; 2012,1(6), 66-69.
- [6] O Innocent;A Emmanuel; A Thomas. *Biosorption of Heavy Metal Ions from Aqueous Solutions Using a Biomaterial. Leonardo Journal of Sciences*; 2009,14 (1), 58-65.
- [7] S Ong; C Seng; P Lim. *Kinetics of adsorption on Cu (II) and Cd (II) from aqueous solution on husk and modified rice husk. Electronic Journal of Environmental, Agricultural and Food Chemistry*; 2007.6 (2), 1764-1774.
- [8] A Bhattacharya;R Venkobachar. *Removal of Cadmium (II) by Low Cost Adsorbents. Journal of Environmental Engineering*; 1984,110 (1); 110–122.
- [9] Bable, S., Kurniawan, T.A.: *Low-cost adsorbent for heavy metals uptake from contaminated water- a review. In: Hazardous Materials. Volume 97 (2003) 219–243.*
- [10] Ferrari, L., Kaufmann, J., Winnefeld, F., Plank, J.: *Interaction of cement model systems with super plasticizers investigated by atomic force microscopy, zeta potential, and adsorption measurements. In: Journal of Colloid Interface Science, Volume 347 (2010) 15–24.*
- [11] A Erto; RAndreozi; ALancia;D Musmarra. *Factors affecting the adsorption of Trichloroethylene onto activated carbons. Journal of Applied Surface Science*;2010, 256 (3), 5237–5242.
- [12] V Leone; S Canzano;P Iovino; S Capasso. *Sorption of humic acids by a zeolite feldspar-bearing tuff in batch and fixed-bed column. Journal of Porous Materials*; 2012,19 (4), 449–453.
- [13]I. Semra, N. Macit, K. Serpil, and O. Huseyin. *Removal of chromium, lead and copper ions from industrial waste water by staphylococcus saprophyticus. Turkish Electronic Journal of Biotechnology. 2:50–57, 2004.*
- [14] K. Amela, Abdeslam H., and M.D. Kerroum. *Isotherm and kinetic study of biosorption of cationic dye onto banana peel. Energy Procedia.*, 19:286–295, 2012.
- [15] M.T. Uddin, M. Rukanuzzaman, M.M.R. Khan, and M.A. Islam. *Adsorption of methylene blue from aqueous solution by jackfruit Artocarpusheteropyllus leaf powder: A fixed-bed column study. Journal of Environmental Management, 90(11):3443–3450, 2009.*

- [16] Z. Zulfadhly, M.D. Mashitah, and S. Bhatia. Heavy metals removal in fixed-bed column by the macro fungus *Pycnoporussanguineus*. *Journal of Environmental Pollution*, 112(3):463– 470, 2001.
- [17] R. Lakshmipathy and N.C. Sarada. A fixed bed column study for the removal of pb (ii) ions by watermelon rind. *Journal of Environ. Sci.: Water Res. Technology*, 1:244–250, 2015.
- [18] Liu, Z., Li, X., Zhan, P., Hu, F. and Ye, X., 2018. Removal of cadmium and copper from water by a magnetic adsorbent of PFM: adsorption performance and micro-structural morphology. *Separation and Purification Technology*, 206, pp.199-207.
- [19] Malik, L.A., Bashir, A., Qureashi, A. and Pandith, A.H., 2019. Detection and removal of heavy metal ions: a review. *Environmental Chemistry Letters*, 17(4), pp.1495-1521.
- [20] Maneechakr, P. and Mongkollertlop, S., 2020. Investigation on adsorption behaviors of heavy metal ions ( $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$ ) through low-cost/active manganese dioxide-modified magnetic biochar derived from palm kernel cake residue. *Journal of Environmental ChemicalEngineering*, 8(6), p.104467.
- [21] Naseem, K., Begum, R., Wu, W., Usman, M., Irfan, A., Al-Sehemi, A.G. and Farooqi, Z.H., 2019. Adsorptive removal of heavy metal ions using polystyrene-poly (Nisopropylmethacrylamideacrylicacid) core/shell gel particles: adsorption isotherms and kinetic study. *Journal of Molecular Liquids*, 277, pp.522-531.
- [22] Ramdani, A., Kadeche, A., Adjdir, M., Taleb, Z., Ikhrou, D., Taleb, S. and Deratani, A., 2020. Lead and Cadmium removal by adsorption process using hydroxyapatite porous materials. *Water Practice & Technology*, 15(1), pp.130-141.
- [23] Salam, O.E.A., Reiad, N.A. and ElShafei, M.M., 2011. A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents. *Journal of Advanced Research*, 2(4), pp.297-303.
- [24] Salishcheva, O.V., Tarasova, Y.V., Lashitskiy, S.S. and Moldagulova, N.E., 2021, February. Analysis of kinetic and equilibrium adsorption of heavy metals by natural materials. In *IOP Conference Series: Earth and Environmental Science* (Vol. 640, No. 6, p. 062007). IOP Publishing.
- [25] Samuel, M.S., Selvarajan, E., Subramaniam, K., Mathimani, T., Seethappan, S. and Pugazhendhi, A., 2020. Synthesized  $\beta$ -cyclodextrin modified graphene oxide ( $\beta$ -CD-GO) composite for cadmium adsorption and toxicity profiles in cervical cancer (HeLa) cell lines *Process Biochemistry*, 93, pp.28-35.