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Column Experiments for Removal of Copper from Wastewater using Activated Carbon Coated with Tio2 Nanoparticles

K. R. Sree Harsha, L Udayasimha, Dharmaparkash, Dinesh Rangappa, Suchetha

Abstract: ***The study reports application of activated carbon coated with TIO_2 nanoparticles to remove Copper from wastewater. The TiO_2 nanoparticles are synthesized using sol-gel process and are coated on Granular Activated Carbon (GAC) using Bisphenol resin as adhesive. The synthesized composite material is characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Column experiments are conducted to investigate removal of copper from industrial effluent by varying flow, height and mass of adsorbent. Results showed decrease in the heavy metal and sorption is well explained by Thomas model.***

Keywords: ***TiO_2 Nanoparticle, Copper, Heavy Metal, Industrial effluent.***

I. INTRODUCTION

Industrial wastewater is often contaminated with various compounds and heavy metals such as phenol, chromium, suspended solids, dissolved organic compounds, copper nickel etc, and it is imperative that it should be treated to an environmental acceptable limit [1].

Adsorption by batch studies forms a basis for initial assessment of the adsorption phenomena. The practical application of using an adsorbent in removing specific pollutants is mainly judged by column experiments as these operations provide efficient utilization of this sorbent material for their maximum adsorption capacity.

The removal of pollutants from aqueous waste stream by adsorption unto granular activated carbon (GAC) in fixed beds is an important industrial wastewater treatment process [2].

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***** Correspondence Author
K. R. Sree Harsha*, *Formerly Research Scholar, B.M.S. College of Engineering, Bangalore-560 019 Presently, Senior Environmental Consultant
L Udayasimha, Professor, B.M.S. College of Engineering, Bangalore – 560019.
Dharmaparkash, Professor, B.M.S. College of Engineering, Bangalore – 560 019.
Dinesh Rangappa, Dean Centre for Nanoscience VTU Regional Campus muddenahalli
Suchetha , Environmental Engineer,Bangalore – 560 019.

In column experiments the solute entering at the inlet end of the column is in continuous contact with the initial layers of the solvent. Therefore, the concentration of the solute which is in contact with a particular layer of the solvent in the column will remain practically constant in the column. This procedure results in loading of maximum sorbent for a uniform solute concentration, whereas, in a batch method there will be continuously declining solute concentration. As the sorbent would have already adsorbed some concentration of the pollutant during the contact time and therefore results in decreased effectiveness of the sorbent. The column studies are best explained by breakthrough curves which are obtained by plotting the effluent concentration of the column with volume of effluent treated or the interval of time taken for treatment, the breakthrough capacity, the degree of column utilization and exhaustion capacity are derived from plotting the breakthrough curves.

Titanium dioxide breaks down almost all organic contaminants. It is also super-hydrophilic and, therefore, is able to adsorb biological contaminants and heavy metal. It is an extensively studied oxide and it is used as model mineral (Journal of Nanomaterials [2]

II. PREPARATION OF SORBENT FOR COLUMN STUDIES:

The sorbent required for column studies are prepared by coating TiO_2 nanoparticles on Granular Activated Carbon (GAC). The TiO_2 nanoparticles are prepared using sol-gel method. Table 1 shows the source of procurement of GAC and its characteristics.

Table1: Properties of granular activated carbon (GAC)

Particulars	Granular Activated Carbon(GAC)
Source	Gowrishankar Chemicals, Tiptur Karnataka, India
Appearance	Black granules
Particle size	4/8 mesh (BSS)
Iodine absorption value	934 mg/gm
Bulk Density	0.556 gm/cc

The coating procedure on GAC involved initial washing of activated carbon with distilled water to remove surface impurities and followed by drying it in sun to remove moisture.

The dried material is soaked in acetone, TiO_2 solution and bisphenol resin overnight. Bisphenol resin acts as adhesive for coating TiO_2 on activated carbon. The entire material is kept in a muffle furnace at 460^0 C for two and half hours under nitrogen atmosphere.

III. ANALYSIS OF SYNTHESIZED MATERIAL

The synthesized material is characterized by subjecting it to X-ray diffraction (XRD) in Rigaku Ultima and scanning (scanning electron microscopy-SEM) through Hitachi SU 1520 model.

Figure 1 represents the synthesized material, i.e, activated carbon coated with TiO_2. Figure 2 shows the XRD spectrums of TiO_2, activated carbon (AC) and composite material GAC coated with TiO_2 (T-AC). The XRD pattern of TiO_2nano particles synthesized by Sol-gel method is presented in Fig. 2 (a). The diffraction peaks appeared at 25.28^0, 37.64^0, 47.84^0, 53.9^0, 62.72^0, and 68.7^0 can be indexed to (101), (004), (200), (105), and (204) planes of the tetragonal crystal structure with anatase phase. The sharp peaks indicated good crystalline property of the prepared TiO_2nano particles. The peaks are well matched with D.B Card NO: 5000223. The pure granular activated carbon spectrum is shown in Fig.2(c). shows peaks at 26.63^0, 50.08^0, 54.79^0,60.03^0which are indexed to (002), (022), (004), (113) planes with graphitic phase. The XRD of TiO_2nano particles coated granular activated carbon(T-AC) is shown in Fig. 2(b) with peaks at 25.28^0, 47.84^0, 53.9^0 belongs to TiO_2nano particles and peaks at 26.63^0, 50.08^0, 54.79^0,60.030belongs to Granular activated carbon. Hence it can be confirmed that TiO_2 nanoparticles is effectively coated on the granular activated carbon surface.

Fig 1: Activated Carbon coated with TiO_2 nanoparticles

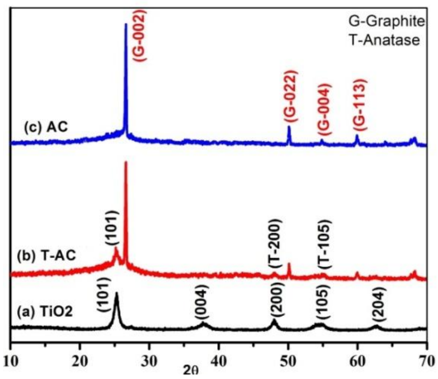

Fig 2: a) XRD spectrum of (a) TiO_2nanoparticles synthesized by Sol-gel method (b) TiO_2 nanoparticles coated granular activated carbon (T-AC) and (c) Granular activated carbon (AC).

Figure 3depicts the SEM Images of the samples. The figures 3a, 3b are the images of GAC with 5µm magnification. It is the porous graphitic surface morphology of GAC. The Figures 3c, 3d are TiO_2 nano particles coated on granular activated carbon (T-AC) with 5µm and 10µm magnification respectively. The images confirmed that irregular shapedTiO_2 nanoparticles are coated on the activated carbon.

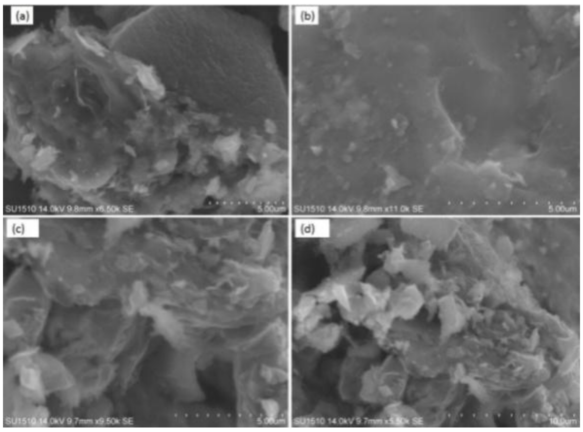

Fig 3: Scanning Electronic Microscopy images of (a-b) Granular activated carbon (AC) and (c-d) TiO_2nano particles coated granular activated carbon (T-AC)

IV. COLUMN EXPERIMENTS AND ANALYSIS

A column set up is fabricated using a source tank for storage of effluent of 5 Lts capacity connected to constant head tank of 2 Lts capacity. They are inter-connected with PVC tubing with pinch cock for controlling the flow rate. The constant head tank has a float arrangement to maintain constant head, which is inturn connected to a column with a support stand and a filtrate collection system. The typical column arrangement is shown in Fig 4.

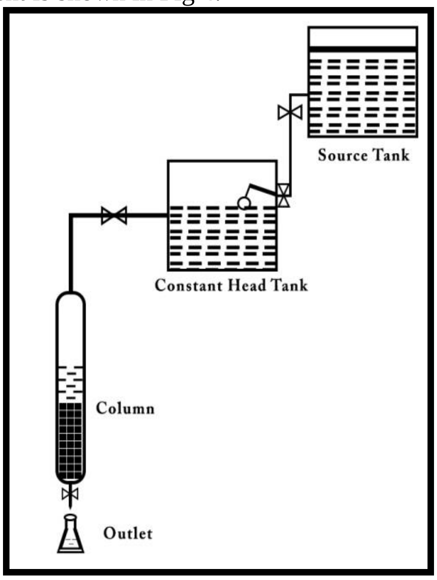

Fig 4: Diagram of Column experimental Set-up

A systematic schedule is planned in assessing the effect of flow rate, height of adsorbent in the column and initial concentration. Twenty-seven experiments are conducted in different combinations as shown in table 2. For each of the experiments, the adsorption behavior is studied through breakthrough curve [Figs 5-13].The details of lag time and saturation time for removal of copper with different experimental variables are represented in table 3. It is observed that the lag time has varied between 15 to 20 minutes and saturation time varied between 65 to 100 minutes.

The copper concentration in all the experiments is reduced and the efficiency of removal is around 95%.

It is observed that as initial concentration of Cu increases lag time decreases in the order of 3-5 minutes. The general observation is that for a given flow rate, lag time (breakthrough time) is noticed to be the same. The lag time is observed to be independent with respect to height of the material in the column and initial concentration of the pollutant. However, as the initial concentration increased (5-15 ppm) for different combination of flow rates and bed heights, the breakthrough time reduced. Hence at lower concentration it showed slightly better adsorption capacity.

As flow rate and bed height increase, the time to saturate the media also increasing

Table 2: Schedule of Experiment

Initial Copper Conc., ppm	Flow Rate Ml/min	Height, cm
5	5	5,10,15
	10	5,10,15
	15	5,10,15
10	5	5,10,15
	10	5,10,15
	15	5,10,15
15	5	5,10,15
	10	5,10,15
	15	5,10,15

Table 3 Analysis of Breakthrough Curve

Initial Copper Conc., C_0ppm	Flow Rate, Q, Ml/min	Height ofbed, h, cm	Breakthrough Time, min	
			Lag	Saturated
5	5	5,10,15	15	70
	10	5,10,15	10	75-82
	15	5,10,15	10	80-85
10	5	5,10,15	18	80-82
	10	5,10,15	10	85-90
	15	5,10,15	10	85-90
15	5	5,10,15	20	85-90
	10	5,10,15	10	90
	15	5,10,15	10	90

V. MODELLING OF EXPERIMENTAL DATA

The column data can be modeled using the theories like Adams–Bohart, Yoon–Nelson and Thomas models [4]. As a preliminary analysis, the sample data is tried with all the above models. Among the three, Thomas model is found to fit the data at satisfactory level. Hence this model is considered for the analysis of the data.

The linearized form of Thomas model can be expressed as,

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{K_{Th} q_0 w}{\vartheta} - K_{Th} C_0 \quad \text{--------1}$$

Where, K_{Th} (mL/min.mg) is the Thomas rate constant; q_0 (mg/g) is the equilibrium Cu uptake per g of the adsorbent; C_0 (mg/L) is the influent Cu concentration; C_t (mg/L) is the effluent concentration at time t and w (g) the mass of adsorbent and υ (mL min-1) the flow rate.

Figure 5 to Figure13 show model prediction and actual experimental observations. Table 4 tabulates the Thomas model parameters for different combinations.

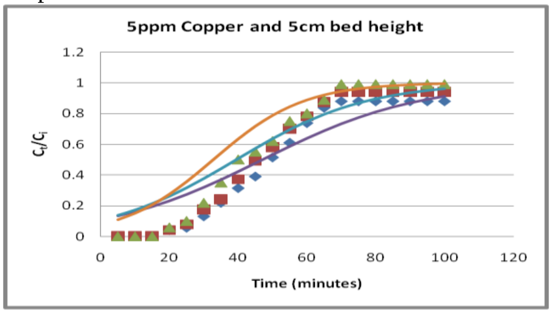

Fig 5: Breakthrough curves and model fit for C_0 = 5ppm and h= 5 cm

Index

Index is same for all the graphs, Figure nos 5-13.

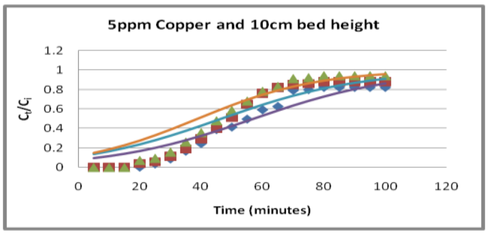

Fig 6: Breakthrough curves and model fit for
C_0 = 5ppm
and h= 10 cm

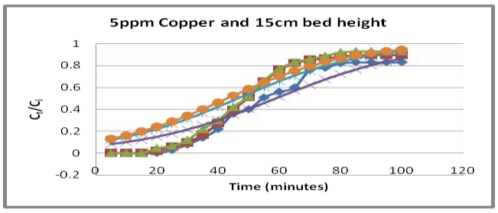

Fig 7: Breakthrough curves and model fit for
C_0 = 5ppm
and h= 15 cm

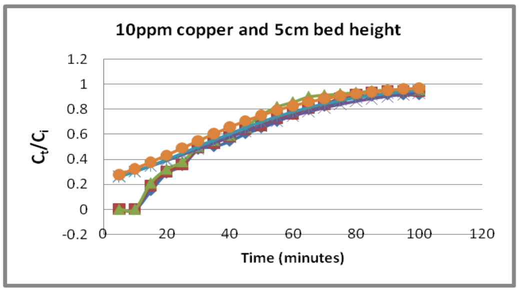

Fig 8: Breakthrough curves and model fit for
C_0 = 10ppm
and h= 5 cm

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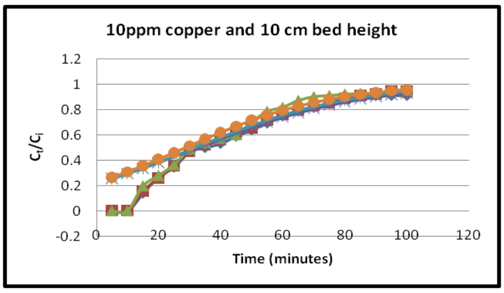

Fig 9: Breakthrough curves and model fit for C_0 = 10ppm and h= 10 cm

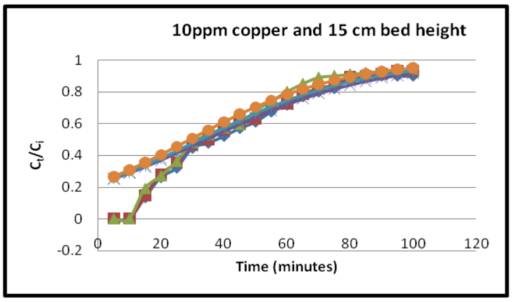

Fig 10: Breakthrough curves and model fit for C_0 = 10ppm and h= 10 cm

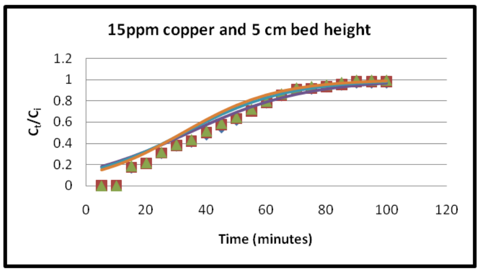

Fig. 11: Breakthrough curves and model fit for C_0 = 15ppm and h= 5 cm

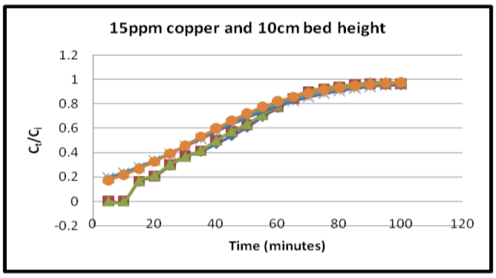

Fig. 12: Breakthrough curves and model fit for C_0 = 15ppm and h= 10 cm

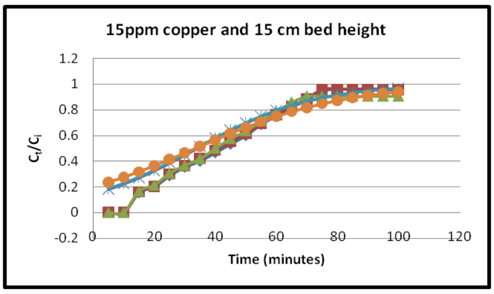

Fig. 13: Breakthrough curves and model fit for C_0 = 15ppm and h=15 cm

Table4: Thomas model parameters of Experimental data

Initial Copper Conc., ppm	Flow Rate Ml/min	Height, cm	Parameters of Thomas Model		
			K_{Th} X10^{-3} (ml/min.mg)	q_o (mg/g)	R^2
5	5	5,10,15	8.8,12, 15.2	113,213, 245	0.62, 0.76 0.79
	10	5,10,15	8.6,8.8, 10.2	107,109 223	0.47 0.62 0.73
	15	5,10,15	9,9.6,10	98,179 218	0.45 0.61 0.68
10	5	5,10,15	3.8,4.2,4.6	158,299, 387	0.87 0.90 0.91
	10	5,10,15	3.8,4,4.3	126,246 331	0.86 0.88 0.90
	15	5,10,15	3.7,3.9,4.2	114,227 293	0.85 0.88 0.90
15	5	5,10,15	3.4,3.8,4.2	254,498 732	0.88 0.88 0.88
	10	5,10,15	3.2,3.4,3.7	201,385 573	0.87 0.88 0.89
	15	5,10,15	3.4,3.4,2.7	173,342 508	0.85 0.86 0.83

From the model analysis of Breakthrough curves obtained at different flow rates (5, 10, and 15 cm) with varying Copper concentration and bed height shows that the R^2 and q_0 values are increased with increase in flow rate and increase in copper concentration and decreased with increase in bed height. Whereas, K_{Th} values are increased with increase in flow rate and bed height and decreased with increase in copper concentration.

The degree of model fitting to the data can be seen with the **coefficient of determination, R^2.** It is observed from the table 4 thatthe R^2 values are improved for 10 and 15 ppm initial concentration of Cu. Hence this can be visualized as a base to scale up the column.

VI. CONCLUSIONS

TiO_2 nanoparticles coated on granular activated carbon (T-AC) effectively, which is proved by XRD.

The efficiency of removal of copper from industrial effluent is 95% for the range of conditions chosen.

The breakthrough time is reduced with respect to increase in pollutant initial concentration for different combination of flow rates and bed heights. Lower concentration showed slightly better adsorption capacity.

Thomas model suited well for the experimental data. As the initial concentration and flow rate increase, the data explained better with the model.

Therefore, the experimental work conducted can effectively applied to address the copper contaminant removal from industrial effluents using TiO_2 nanoparticle coated GAC.

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AUTHORS PROFILE

Dr. K.R. Sree Harsha received his bachelors' degree in Civil and Environmental Engineering from university of Mysore and obtained his masters degree in Environmental Engineering from Visveswaraiah Technological University, Belgaum, Karnataka in 2008.He has completed his PhD from BMSCE, Bengaluru as research center under Visveswaraiah Technological University, Belgaum, Karnataka in 2018. Since obtaining his bachelor's degree, he has been practicing as Environmental consultant and has designed and installed water and wastewater treatment facilities including Multi effect evaporator (MEE) and air pollution control devices. In his capacity as environmental consultant, he has provided consulting services for preparation of environmental impact assessment reports of different sectors covered under EIA notification and has to his credit many contracts in government and private sector.