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REMOVAL OF COPPER IONS FROM WASTE WATER BY WASTE TIRE RUBBER

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Abstract: The effluent stream released from the industries mainly comprises of hazardous chemicals and heavy metal ions. Copper is abundant in nature and has a dominant presence in most of the effluent streams containing Cu (II). The electroplating and steel industries effluents are the major source for the Cu (II) production in wastewater streams. The present study showed that waste tire rubber ash was capable of removing copper ions from industrial wastewater samples. These are activated by giving the heat treatment. Continuous adsorption studies demonstrate that the adsorbents have a significant capacity for adsorption of Cu (II) from steel plating industry. The effects of inlet Cu (II) concentration (5-15 mg/l), feed flow rate (10-30 ml/min) and WTR bed height (10-20 mm) on the breakthrough characteristics of the adsorption system were determined. The cost of removal is expected to be quite low, as the adsorbent is cheap and easily available in large quantities. The adsorption data were fitted to two well-established fixed-bed adsorption models namely, Adam-Bohart and Thomas models.

Key words: wastewater, continuous process, waste tire rubber ash, Adam-Bohart and Thomas models.

I INTRODUCTION

Water is one of the most important elements on earth. Every living being needs water for its survival. Water of high quality is essential for life and water of acceptable quality is essential for agriculture, industrial, domestic and commercial uses. The increase in the utilization of fresh water for industrial purposes is a serious problem now-a-days which is faced by all through the world. The wastewater streams released from industries are contributing in contaminating the fresh water available in nature, depletion of the fresh water and increasing the water pollution. The effluent stream released from the industries is mainly comprised of hazardous chemicals and heavy metal ions such as chromium, nickel, copper, lead, arsenic, etc. Heavy metals are very toxic in nature and harmful to the environment. The increasing contamination of urban and industrial wastewaters by toxic metal ions causes significant environmental pollution. This results in the pollution of water whereby the quality of water deteriorates, affecting aquatic ecosystems. Copper and its compounds are widely used in many industries and there are many potential sources of copper pollution. The continued intake of copper by humans leads to necrotic changes in the liver and kidney, mucosal irritation; wide spread capillary damage, depression, gastrointestinal irritation, and lung cancer. According to the Safe Drinking Water Act, the permissible limit of copper in drinking water is 1.3 mg/L.6 Excessive copper concentrations can lead to weakness, lethargy and anorexia, as well as damage to the gastrointestinal tract Therefore, there is a considerable need to treat industrial effluents containing such heavy metals prior to discharge to protect public health. The metal needs to be removed from industrial effluents before discharge into the environment to mitigate any impact on plant, animal and human receptors.

In recent years, adsorption was shown to be an economically feasible method for the removal of metal ions from water and wastewater. The biggest barrier in the industrial application of this process is the high cost of adsorbents presently available for commercial use. The cost of the application of adsorption technologies can be reduced if the adsorbent is inexpensive. hence, the search for low-cost adsorbents that have metal-binding capacities has intensified. This has led many workers to search for cheaper alternatives among plant wastes or industrial by-products, such as granular red mud, chitosan, potato peel, fired coal fly ash, sugar beet pulp.

Waste tires have been a major management and disposal problem in many countries for decades. Many waste tires are currently stockpiled in various countries around the globe. These stockpiles are dangerous because they pose a potential environmental concern, are fire hazards and provide breeding grounds for mosquitoes. The practice of disposing waste tires in landfills is becoming unacceptable because of the rapid depletion of available landfill sites.

This work is focused on the removal of Cu(II) ions from aqueous solutions using waste tire rubber ash (WTRA) as an adsorbent. The influences of pH, contact time, initial iron concentration, temperature and adsorbent dosage on the removal of Cu(II) from wastewater and water solutions were investigated. Equilibrium isotherm data were analyzed by the Langmuir and Freundlich equations using linear regression analysis. The adsorption efficiency towards copper ion removal was tested using different industrial wastewaters.

In this work, waste tire rubber is used as precursor for preparation of activated carbon for Cu (II) removal from sample solution by fixed-bed column. The important design parameters such as inlet concentration of Cu (II) solution, flow rate of fluid and column bed height were investigated. The breakthrough curves for the adsorption of Cu (II) were analyzed using Adam-Bohart, Thomas and Yoon-Nelson models.

II MATERIALS AND METHODS

The waste water was taken from the local metal plating industry. It had a pH of 4.5 and contained Cu (II) at a concentration of 2 mg/l by using Atomic Adsorption Spectrophotometer.

Samplecollection:

ADSORBENT PREPARATION & CHARACTERIZATION:

Waste tire rubber ash was first washed with detergent solution and dilutes HCl in order to remove soil debris. Then the clean and dry parts were burnt and the residue was taken in crucible and burnt completely at 500 °C in a muffle furnace for few hours. The cooled ash was then washed with a very dilute acidic solution, to remove salts of metals and the mixture was filtered out using a Whatman filter paper. Then the activated waste tire ash is washed with the distilled water to remove the free acid and dried for few hrs.

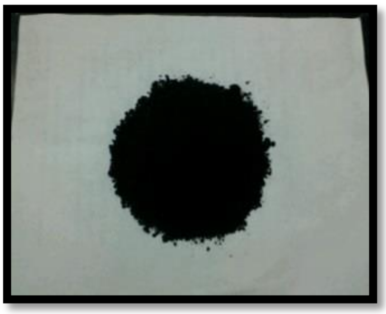

Fig -2 activated waste tire rubber

The adsorbent samples were characterized by Scanning Electron Microscope (SEM). The scanning electron micrograph (SEM) images of activated carbons allowed us to visualize and assess the surface chemistry of sample. The surface texture and porosity are clearly indicated after the carbonization. This figure shows that the active carbon absorbent issued from regularly porous surface, indicating a high surface area of mesoporous dimensions. The SEM has also enabled us to evaluate an average pore size, less than 100 nm and less than 60 nm for activated carbon

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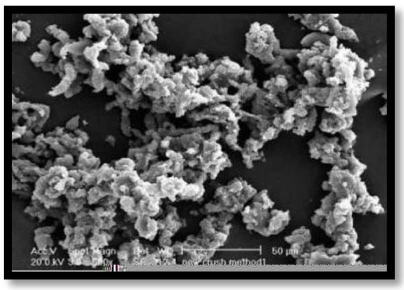

Fig- 3 SEM image for WTR

Continuous Adsorption Studies

The continuous adsorption studies were conducted in a glass column with internal diameter of 1.5 cm and length of 40 cm. The packed bed between the glass wool and glass beads in order to prevent the wash out of the adsorbent. Packed bed experiments were carriedout at 25°C. A known quantity of adsorbent was then placed in the column to yield the desired bed height (25 cm and 15 cm) of the adsorbent. Experimentswere conducted to study the effect of bed height, flowrate of the influent metal solution at a fixed initial concentrationof metal in influent.Pretreated adsorbent of 1, 2 and 3 g were packed in the glasscolumn and the sorption experiment was performed correspondingto 2.1, 3.1 and 4.1 cm of initial height of the column. Thesorption was conducted at flow rates between 1.6 and 9.8 ml/min. Cu (II) solution of concentration 10 mg/l, was fed from the top of the column. Effluent samples were collected at different times from the bottom of the column. Column effluent samples were analyzed by atomic absorption spectroscopy. Operation of the column was stopped when the effluent Cu (II) ion concentration expected to removed maximum of its initial concentration.

Column model

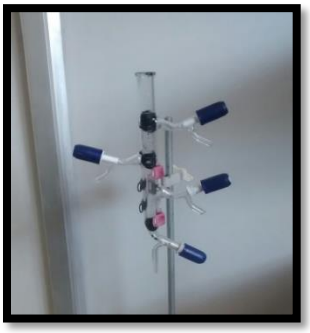

Fig- 4 Fixed bed column

The loading behavior of Cu (II) to be removed from solution in a fixed bed was usually expressed in term of C_t/C_O where (C_t = effluent Cu (II) ion concentration and C_O= influent Cu (II) ion concentration in mg/ l). C_t/C_O is then plotted against time in other to obtain breakthrough curve. The maximum column capacity, q_{total} (mg), for a given feed concentration and flow rate is equal to the area under the plot of the adsorbed Cu (II) concentration, C_{ad} (C_{ad} = C_O -C) (mg/l) versus effluent time (t, min) and is calculated from

$$q_{total} = \frac{QA}{1000} = \frac{Q}{1000}\int_{t=0}^{t=total} C_{ad}\, dt$$

where t_{total}, Q and A are the total flow time (min), volumetric flow rate (ml/min) and the area under the breakthrough curve, respectively. The equilibrium uptake ($q_{eq(exp))}$) is calculated as follows

$q_{ep(exp)} = \frac{q_{total}}{m}$ where mis the total dry weight of WTR in column (g). The total amount of Cu (II) sent to the column (W_{total}) is calculated from equation below

$$W_{total} = \frac{C_O Q_{total}}{1000}$$

Total removal percent of Cu (II) is the ratio of the maximum capacity of the column (q_{total}) to the total amount of Cu (II) sent to column (W_{total})

$$Y = \left(\frac{q_{total}}{W_{total}}\right) \times 100$$

For the successful design of a column adsorption process, it is important to predict the breakthrough curve for effluent parameters.

Various kinetic models have been developed to predict the dynamic behaviour of the column.

III RESULTS AND DISCUSSION

Table 4.1.1 Cu (II) adsorption at different inlet concentrations (bed height = 20 mm, flow rate = 10 ml/min, temperature = 25°C)

INITIAL CON C_O (mg/l)	TIME (min)	FINAL CON C_t (mg/l)	C_t / C_O	% REMOVAL (Y)
5	30	3	0.60	40
	60	2.5	0.50	50
	90	2.3	0.46	54
	150	2	0.40	60
10	30	3.5	0.35	65
	60	3.1	0.31	69
	90	2.85	0.29	71.5
	150	2.8	0.28	72
15	30	3.88	0.26	74
	60	3.50	0.23	77
	90	3.21	0.21	78
	150	3.10	0.21	79

Table 4.1.2 Cu (II) adsorption at different flow rates (Cu (II) inlet concentration=10 mg/l, bed height = 20 mm, temperature = 25°C).

FEED FLOW RATE (ml/min)	TIME (min)	FINAL CON C_t (mg/l)	C_t / C_O	% REMOVAL (Y)
10	30	3.5	0.35	65
	60	3.1	0.31	69
	90	2.85	0.29	71.5
	150	2.8	0.28	72
20	30	3.2	0.32	68
	60	2.95	0.30	71
	90	2.50	0.25	75
	150	2.48	0.25	75
30	30	3.15	0.32	69
	60	2.8	0.28	72
	90	2.51	0.25	75
	150	1.85	0.19	81

Table 4.1.3 Cu (II) adsorption at different bed height (Cu (II) inlet concentration = 10 mg/l, flow rate = 10 ml/min and temperature = 25^{O}C).

WTR BED HEIGHT (mm)	TIME (min)	FINAL CON C_t (mg/l)	C_t / C_O	% REMOVAL (Y)
10	30	3.2	0.32	68
	60	3	0.30	70
	90	2.5	0.25	75
	150	2.1	0.21	79
15	30	3	0.30	70
	60	2.50	0.25	75
	90	2	0.20	80
	150	1.80	0.25	82
20	30	2.84	0.32	72
	60	2.75	0.28	73
	90	2.20	0.25	78
	150	1.65	0.19	84

Fig-5 fixed bed column with wastewater

Fig -6 fixed bed column with wastewater

Kinetic models

The Adam-Bohart model is used for the description of the initial part of the breakthrough curve. The expression is expressed as

$$\frac{C_t}{C_0} = exp\left(k_{AB}C_0t - k_{AB}N_0\frac{Z}{F}\right)$$

Where k_{AB} is the kinetic constant (l/mg min), Fis the linear flow rate (ml/min), Zis the bed depth of column (cm), N_0 is the saturation concentration (mg/l) and tis time (min). Parameters describing the characteristic operations of the column ($k_{AB}$and N_0) were calculated using linear regression analysis according to above Equation.

From a linear plot of ln (Ct/Co) against time (t), values of $K_{AB}$and N_0 were determined from the intercept and slope of the plot.\

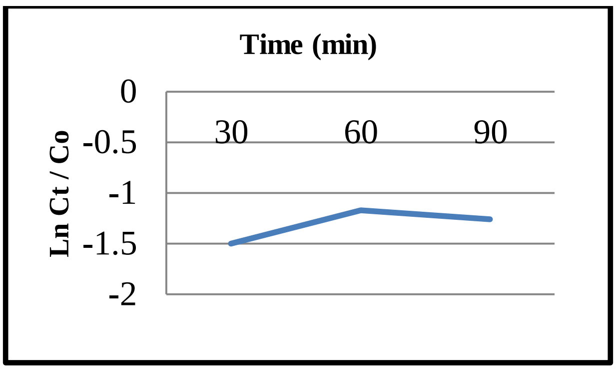

Fig – 7 Adam-Bohart model for Cu (II) adsorption

The expression of Thomas model for an adsorption column is given as follows

$$\frac{C_t}{C_0} = \frac{1}{1 + exp\left(\frac{k_{Th}q_0 m}{v} - k_{Th}C_0 t\right)}$$

Where $q_o$the equilibrium Cu (II) uptake per g of the WTR adsorbent (mg/g). The values of $K_{Th}$and $q_o$were determined from a plot of C_t/ C_O against t using linear regression analysis.

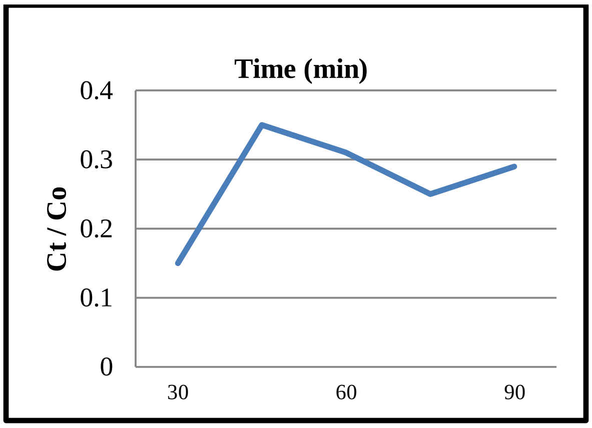

Fig – 8 Thomas model for Cu (II) adsorption

4.2.3 Isotherm constants for Cu (II) adsorption

Ion	Adam-Bohart model			Thomas model		
Cu	k_{AB}	N_0	R^2	K_{Th}	q_o	R^2
(II)	2.2	91.4	0.90	0.68	25.26	0.97

From fig 4.2.1 and fig 4.2.2 shown that the adsorption data were fitted to different isotherm model equation and the Thomas model was found to be the best model for Cu i.e R^2 value is 0.97

IV CONCLUSION

The present study show that the activated carbon prepared from chemically treated waste tire rubber ash (WTRA) is an effective adsorbent for the removal of copper ions from collected waste water. Influence of process parameters such as pH, inlet Cu (II) concentration, feed flow rate and WTR bed height were at moderate levels such that they can affect the removal efficiencies of the heavy metals were concerned.

In this continuous process the effects of inlet Cu (II) concentration (5-15 mg/l), feed flow rate (10-30 ml/min) and WTR bed height (10-20 mm) on the breakthrough characteristics of the adsorption system were determined. The result was obtained using 10 mg/l inlet Cu (II) concentration, 20 mm bed height and 10 ml/min flow rate.

The result would be useful for the waste water treatment plants for the removal of copper. The results of the present study concluded that activated waste tire rubber ash (WTRA) is the suitable adsorbent for the removal of Copper. Activated waste tire rubber ash (WTRA) could be used as low cost adsorbents in effective effluent treatment, especially for the removal of metal ions. The results will be highly useful in the low cost treatment plants.

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