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Reclamation of Copper from Electronic Industry Effluent Using Plant Root Adsorbent

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Abstract : Copper ion contamination in electronic industrial effluent is an universal issue. The traditional way of copper removal from effluent have some disadvantages like expensive operational cost, sludge generation after water treatment. Adsorption technique for copper(II) using synthetic adsorbent is one of the efficient ways of water treatment but it is expensive on a commercial scale. Due to this, researcher across the globe is looking after to find the efficient, economical, and readily available biomass-based adsorbent for metal recovery. The present study was intended for adsorption of copper on to Datura (*Datura stramonium*) root powder using batch studies. It was found to be one of the efficient bioadsorbent with 947 mg/g copper adsorption capability. Batch experiments were performed by using 4 g/L of Datura root powder kept in contact with 100 ppm copper containing industrial effluent in 15 min contact time at pH 4. The result indicates 95% copper adsorption on the surface of Datura root powder. Kinetic study indicates that experimental data fit well in pseudo second order rate reaction and follows Freundlich isotherm indicating multilayer adsorption process. FT-IR result indicates involvement of aromatic group (Phosphates) of Datura root binding with copper ions. Elution experiments were performed using 10% H_2SO_4 in 60 min to remove copper from loaded adsorbent. High copper adsorption capacity and its regeneration efficiency of Datura root powder suggest its applicability in copper reclamation from electronic industrial effluent.

Keywords: *Bioadsorbent, Datura Root Powder, Heavy Metals, Industrial Effluents, Copper.*

1. INTRODUCTION :

Water pollution due to heavy metal discharge in it is major environmental problem that causes various harmful effects for both human being and animals. Accumulation of such toxic metals in to body may create many health related issue like anaemia, kidney and liver dysfunction, brain damage, nausea, skin irritation, etc. and it may be lethal in some cases [1]. Primary source of these heavy metals are electroplating, textile and surface finishing industries. Mostly, these metals are difficult to degrade in natural way so goes on accumulating in the food chain and ultimately in human body. So, it is necessary to remove heavy metal from both effluent discharge and drinkable water for the maintenance of healthy environment [2].

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There are various technologies available for heavy metal removal from effluents such as coagulation, flocculation, membrane filtration, reverse osmosis, precipitation, advanced oxidation, ion exchange, evaporation, and adsorption. Unfortunately, all the available technologies suffer from certain disadvantages including high energy consumption, process and maintenance cost, availability, generation of harmful side products, inadequate elimination, etc [3]. Besides that bioadsorption process via live or dead biomasses is cost effective way for effluent treatment for metal recovery. In this point of view, bioadsorbent serve as a substrate for metal binding with various functional groups. High efficiency, availability, low cost, no hazardous by-products are some of the major advantages of this technique. Commonly, these bioadsorbent includes agricultural waste, plant, animal, algae, fungi biomass as an adsorbent [4]. Datura *(Datura inoxia)* plant leaf based adsorbent was shown high adsorption potential for recovery of cadmium, chromium and lead from effluent [5]. While, Datura *(Datura stramonium)* fruit was shown 44.34 mg/g adsorption capacity for chromium from waste water [6]. But surprisingly very few literatures were available on root based adsorbent for the recovery of different heavy metals.

Present study deals with Datura *(Datura stramonium)* root powder as an adsorbent for copper recovery from industrial effluent. Different process parameters in batch studies, like effect of contact time, adsorbent dose, pH of the solution, metal concentration in aqueous feed, etc. have been studied and optimized for the maximum adsorption of copper from the industrial effluent.

2. EXPERIMENTAL SECTION

2.1. Materials

The industrial waste water with 50- 300 ppm range copper was used for performing experiments. Initially, synthetic solution of copper in sulfate medium was prepared which had similar concentration of copper as electronic industrial effluent. Datura root was collected from road side bushes for preparing its powder. Laboratory grade chemicals like copper sulfate, hydrochloric acid, sulfuric acid, ammonium hydroxide required for experimental purpose were purchased from E. Merck, India.

2.2. Method

2.2.1. Preparation of adsorbent

Datura plants were collected from road side dumped area. Roots were separated from stem and leafy part of the Datura plant. Separated roots from Datura plant were washed completely using tap water to washout trapped soil particles to the Datura roots and then washed using distilled water for complete cleaning process. These Datura roots were reduced in size of 5 to 6 mm by cutting it into small pieces and then kept in an oven at 150^{o}C for 5-6 h until removal of complete moisture [5]. Then root sample was grinded in to mortar and pestle to prepare fine Datura *(Datura stramonium)* root powder. This Datura root powder was used as it is (without any chemical activation) for adsorption studies.

2.2.2. Adsorption and elution method

The batch experiments were performed in a conical flask (Capacity: 100 mL) at normal atmospheric temperature using copper solution and Datura root powder in different proportion and mixed constantly by using wrist action shaking machine. During the adsorption experiments, various parameters like pH, adsorbent dose, time etc., were studied. The pH was maintained in between 1 to 6 using dil. acid (H_2SO_4) or base (NH_4OH). The loaded adsorbent was eluted using 10% (v/v) H_2SO_4 to get pure and concentrated copper solution and Datura root powder was regenerated and re-used for further experiments.

2.2.3. Analytical method

Copper concentration in the aqueous solution was measured by Atomic adsorption spectrophotometer (AAS) (Perkin Elmer model, Analyst 200; USA) using 324.8 nm wavelength. Equilibrium pH of aqueous feed solution was adjusted using CL 46 pH meter (Toshniwal Pvt. Ltd., Ajmer) for maximum copper adsorption on adsorbent. Fourier Transform Infrared Spectroscopy (FT-IR NICOLET 5700, Thermo Electron Corporation, USA) was used to study changes in fresh and copper loaded Datura root powder peaks due to adsorption.

Adsorption capacity was obtained from Eq. (1) as follows;

Adsorption Percentage (%): $[(C_o - C_e)/C_o] \times 100$ (1)

Adsorption capacity of Datura root powder was calculated by using equation (2) as follows;

Adsorption capacity (q_e): $[(C_o - C_e)/m] \times V$ (2)

Elution efficiency was calculated by using equation (3) as follows;

Elution Percentage (%): $[C_f/(C_o - C_e)] \times 100$ (3)

Where,

C_o: Copper concentration in aqueous feed solution (ppm)

C_e: Copper concentration in the raffinate after adsorption process (ppm)

C_f: Copper concentration in elutant after acid treatment (ppm)

m: Adsorbent mass (g)

V:Adsorbent Volume (L) [7,8]

3. RESULTS AND DISCUSSION

To reclaim copper from electronic industrial effluent, experiments were carried out for copper adsorption using Datura root powder as an adsorbent from the synthetic copper solution in sulfate medium, which was similar to effluent. Different process parameters like contact time, pH, adsorbent dose, copper concentration in aqueous feed were altered for adsorption studies.

3.1. Effect of contact time on copper adsorption

Adsorption of copper on Datura root powder at various contact time were studied from 2.5 to 15 min, while other parameters kept constant. Experiments were performed using 0.2 g Datura root powder in 50 mL of aqueous feed copper solution to maintain 4g/L adsorbent dose (3 set: 50, 100 and 150 ppm of copper in feed). Results indicated that adsorption percentage increases with increase in time of contact on adsorbent and number of adsorbate remain in the solution until equilibrium was attained [2]. It states that 15 min contact time was sufficient for maximum adsorption of copper from all 3 experimental conditions (Figure 1). Therefore, 15 min contact time was selected for further batch experiments.

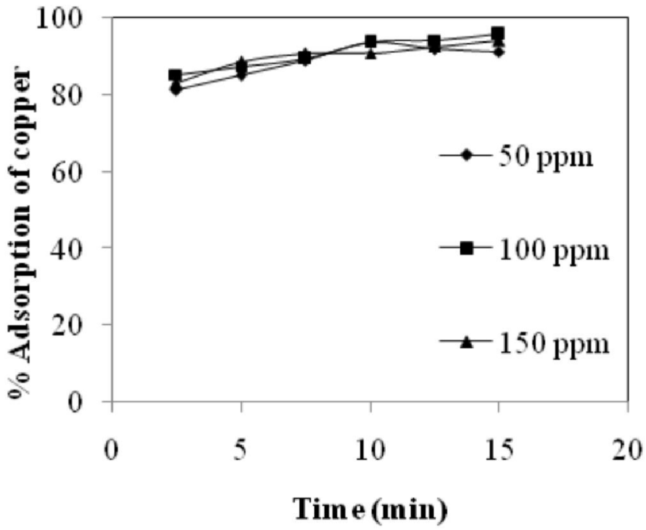

Figure 1. Effect of contact time (Adsorbent: Datura root powder: 0.2 g/ 50 mL of feed solution; Aq. feed concentration: 50, 100, 150 ppm of Cu;Initial pH:4)

3.2. Effect of adsorbent dose on copper adsorption

To study the adsorption behavior of copper, adsorbent dose was changed from 0.05 to 1 g keeping other parameters constant. Experiments were carried out using the aqueous feed with 50,100 and 150 ppm copper concentration and contact time of 15 min at pH 4.0. Result indicated that 0.2 g of Datura root powder was sufficient for more than 90 % of adsorption within contact time of 15 min in all three aqueous feed solutions i.e.50, 100, 150 ppm copper concentration (Figure 2). Increase in adsorbent dose leads to increase in adsorption of copper ions as no. of sites available for adsorption of metal increases [9]. It gave idea about minimum amount of adsorbent required for maximum adsorption process. Hence, further experiments were carried out with 0.2 g adsorbent dose per 50 mL of feed solution (4 g/L).

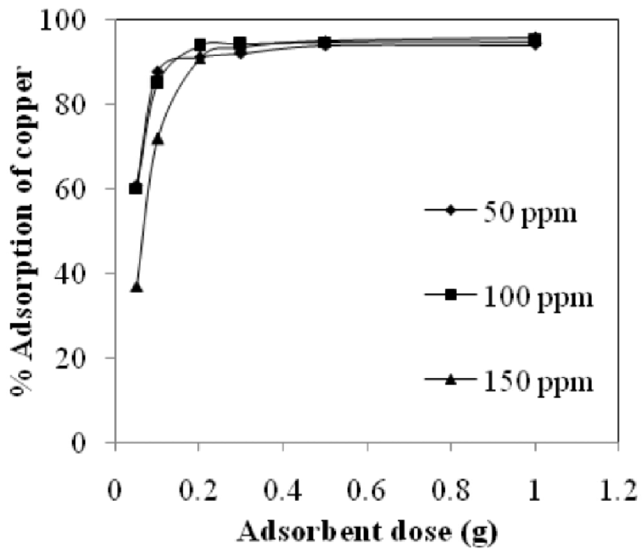

Figure 2. Effect of adsorbent dose (Adsorbent: Datura root powder; Aq. feed concentration: 50, 100, 150 ppm of Cu; Contact time: 15 min;Initial pH: 4.0)

3.3. Effect of pH on copper adsorption

Effect of pH on adsorption of copper was studied in a pH range varying from 1.0-6.0 to adsorb the copper from 50 mL of effluent (containing 100 ppm copper) using 0.2 g Datura root powder as an adsorbent in contact time of 15 min. Result shows that copper adsorption increases from 5.82 % to 94 % with increase in pH from 1.0 to 4.0, while adsorption efficiency was decreased to 55.85 % at pH 6.0 (Figure 3). It may be due to change in the nature of adsorbent surface and its ionization capacity. Below the pH 4.0, H_3O^+ ions from aqueous feed solution compete with the copper ions for binding with surface site of Datura root powder. While, above the pH 4.0, it shows precipitation of copper as a copper hydroxide resulting in the decrease of copper adsorption percentage [10]. Hence, pH 4.0 has been considered optimum for adsorption of copper from effluent.

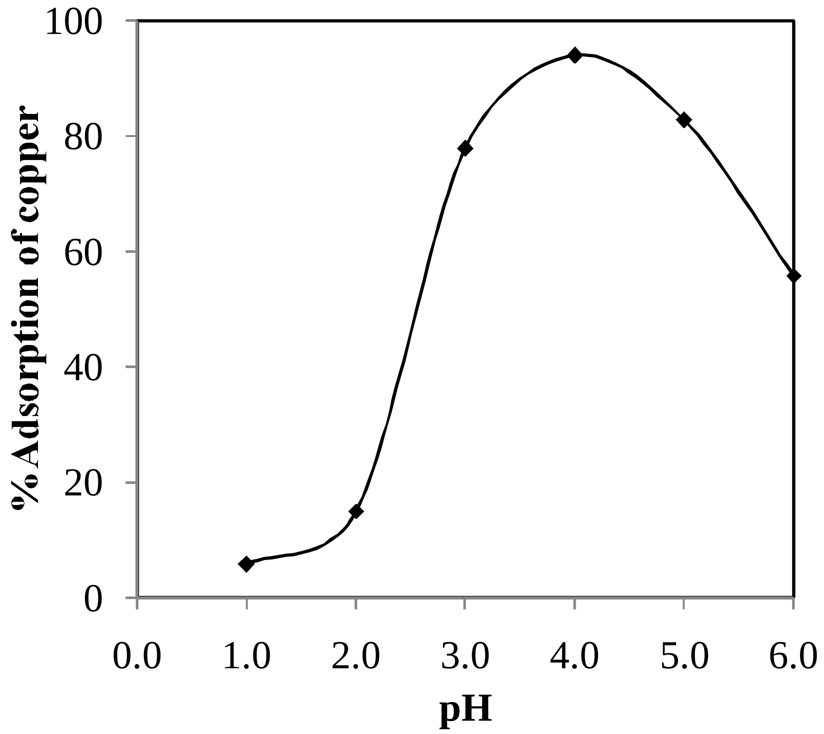

Figure 3. Effect of pH (Adsorbent: Datura root powder: 0.2 g/ 50 mL of feed solution; Contact time: 15 min; Aq. feed concentration: 100 ppm of Cu).

3.4. Effect of aqueous feed concentration of copper

Effect of aqueous feed concentration on adsorption of copper was studied by using 0.2 g of adsorbent in 50 mL of different copper concentration in the range of 50 to 300 ppm. Result indicated that copper adsorption decreases from 93.76 to 65 % with increase in aqueous feed copper concentration from 100 ppm to 300 ppm (Figure 4). It may be due to increased copper ions with respect to available adsorbent/adsorption site so probability of binding of copper ions to adsorption site decreases with increase in aqueous feed concentration. Adsorption efficiency decreases at higher metal concentration due to the saturated exchange sites of adsorbent [11]. According to results, 100 ppm copper concentration showed maximum adsorption at optimized parameters so it was considered for loading capacity experiments.

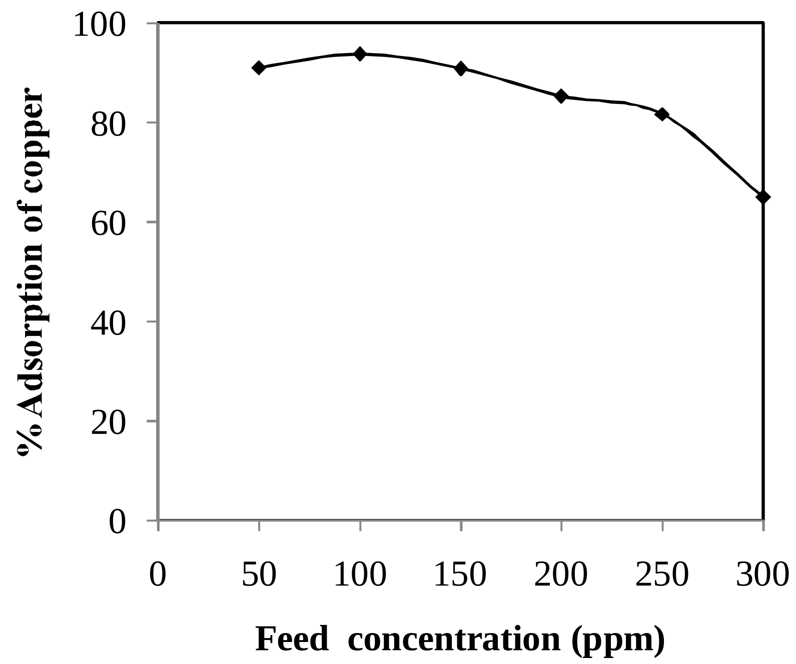

Figure 4. Effect ofAq. feed concentration (Adsorbent: Datura root powder: 0.2 g/50 mL of feed solution; Contact time: 15 min; Initial pH: 4.0)

3.5. Loading capacity of Datura root powder

In order to determine the maximum loading capacity of adsorbent Datura root powder, the repetitive contacts of the effluent was made with the same adsorbent. It was calculated by feeding fixed copper solution to same adsorbent multiple times. Result indicates that, 4^{th}contact of fresh 50 mL of 100 ppm copper solution was sufficient to complete saturation of adsorption site i.e. 189.4 mg of copper on 0.2 g of Datura root powder (Figure 5). It indicated that adsorption site of adsorbent was fully occupied with copper ions [12]. This data was used to calculate adsorption capacity of Datura root powder i.e. 947 mg/g of adsorbent.

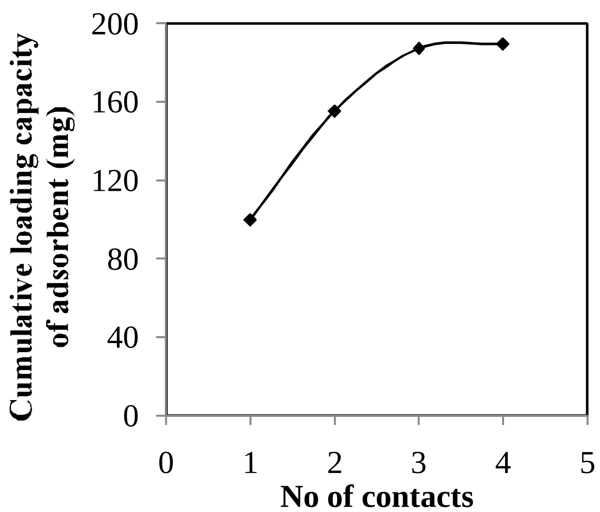

Figure 5. Cumulative loading capacity of adsorbent (Adsorbent: Datura root powder: 0.2 g/ 50 mL of feed solution; Contact time: 15 min; Initial pH: 4.0).

3.6. Elution of copper from loaded adsorbent

Acid concentration played significant role in elution of copper from the loaded adsorbent. Sulfuric acid was found to be best for the elution amongst all acids[13]. Therefore, effect of different sulfuric acid concentration on elution of copper from loaded adsorbent was checked. Experiments were performed using 0.2 g of 95 % loaded adsorbent kept in contact with 50 mL of different sulfuric acid concentration (1 to 10%) with shaking time of 60 min. Result indicated that increase in acid concentration from 1 to 10%, increases elution percentage from 77.64 % to 100% from the loaded adsorbent (Figure 6). It indicates that copper was eluted completely from the loaded adsorbent in contact with 10% sulfuric acid concentration for 60 min.

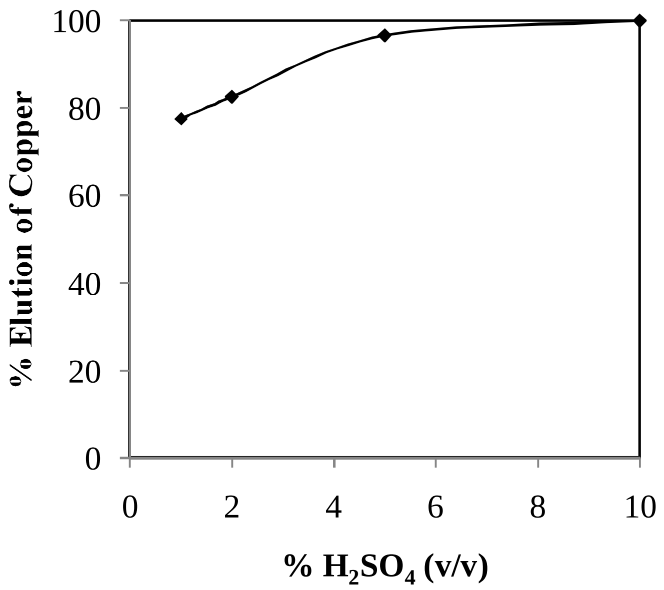

Figure 6. Effect of acid concentration on elution of copper from loaded Datura root powder (Loaded Adsorbent: Datura root powder: 0.2 g/ 50 mL of acid solution; Contact time: 60 min)

3.7. Adsorption kinetics and isotherm for copper adsorption on Datura root powder

3.7. 1. Adsorption kinetics

Experimental outcome obtained from the copper adsorption on 0.2 g of Datura root powder 50 mL of from aqueous feed concentration of 50-150 ppm in different contact time from 2.5 to 15 min was used to determine adsorption kinetics. Pseudo first order and pseudo second order are well proven kinetic expression [6] utilized to fit experimental results (Table 1).

Graphs were drawn by using these results for both order of reaction (Figure 7 (a), 7 (b)). k_1 and k_2 values were calculated from the slopes obtained from the graphs. These values along with correlation coefficient R^2 is enlisted in Table 1.

Comparing both order of reaction, pseudo second order rate reaction shows 0.99 correlation coefficient in all 3 experimental condition (50, 100, 150 ppm copper in aqueous feed). Hence pseudo second order reaction fits well with experimental results.

Table 1. Kinetic equations and rate constants for different rate reactions for the adsorption of copper on Datura root powder

Adsorption Kinetics	Equation	Description	Conc. in Aq. Feed (ppm)	k_1/k_2	R^2
1st order equation	$dqt/dt = k_1 (q_e - q)$	q_e: Copper adsorbed on the adsorbent at equilibrium (mg/g) q: Copperadsorbed on the adsorbentat time t (mg/g) k_1: Pseudo first order Rate constant (g/mg min)	50 100 150	0.154 0.223 0.181	0.873 0.937 0.951
2nd order equation	$dqt/dt = k_2 (q_e - q)^2$	k_2: Pseudo second order Rate constant (g/mg min).	50 100 150	0.0686 0.0730 0.205	0.999 0.999 0.998

3.7.2. Adsorption isotherm

Langmuir and Freundlich adsorption isotherm were utilized for analysis of copper adsorption data on 0.2 g Datura root powder. It was kept in contact with 50 mL of copper solution for 2.5 to 15 min time interval (50, 100, 150 ppm copper in aqueous feed). Langmuir adsorption isotherm states monolayer adsorption on homogeneous adsorbent surface, while Freundlich adsorption isotherm states multilayer adsorption on heterogeneous adsorption surface. These well known adsorption isotherm equations [6] are mentioned in Table 2.

Graphs were drawn by using these results for both isotherm model (Figure 7 (c), 7 (d)). k_l and k_f values were calculated from the slopes obtained from the graphs. These values along with correlation coefficient R^2 are enlisted in Table 2.

Comparing both isotherm models, Freundlich adsorption isotherm shows more than 0.96 correlation co-efficient in all 3 experimental conditions (50, 100, 150 ppm copper in aqueous feed). Hence Freundlich adsorption isotherm is well suited with experimental results indicates multilayer adsorption of copper ion on heterogeneous surface of Datura root powder.

Table 2. Adsorption isotherm equations and rate constants for copper adsorption on Datura root powder.

Adsorption isotherm	Equation	Description	Conc. in Aq. feed (ppm)	q_m(mg/g)	k_1	R^2
Langmuir adsorption isotherm	$1/q = [(1/k_1.q_m)\ (1/C_e) + (1/q_m)]$	q: Copper metal adsorbed on adsorbent at equilibrium.	50	9.523	5138.74	0.899
		k_1: Langmuir constant	100	20	2500	0.897
		q_m: The adsorbent capacity (Maximum adsorption of copper metal on adsorbent in mg per unit mass of adsorbent in grams)	150	26.31	1900.4	0.856
		C_e: Equilibrium copper concentration in the raffinate (mg/L)				
Freundlich adsorption isotherm	$q = k_f \times (C_e)^{1/n}$	k_f: Freundlich constant/ Constant related to the affinity of binding sites for the copper.	**Conc.in Aq. feed (ppm)**	**n**	**k_f**	**R^2**
		n: Freundlich exponent.	50	0.195	5.321	0.975
			100	0.098	13.64	0.971
			150	0.123	17.10	0.965

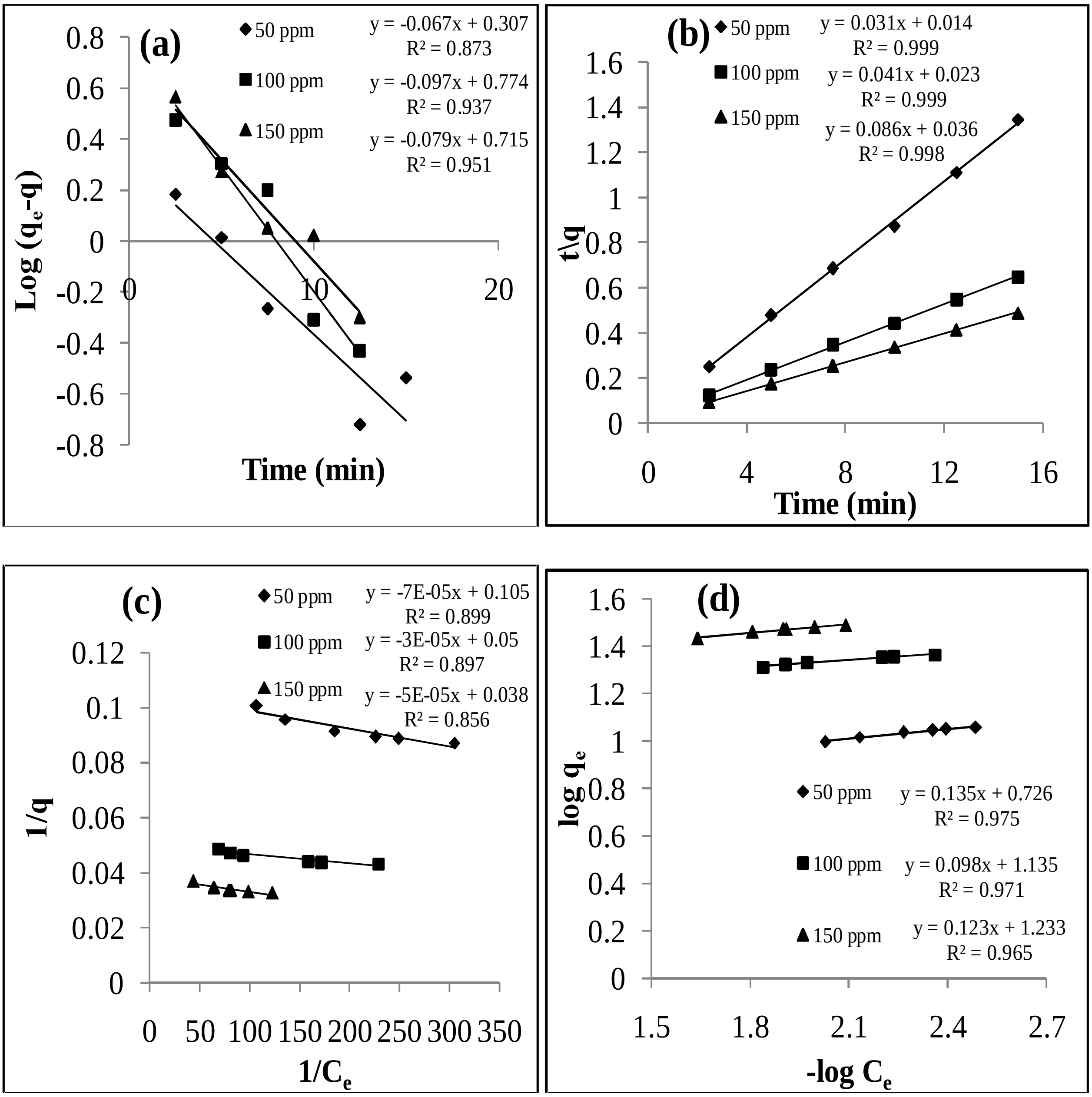

***Figure 7.** (a) 1st order equation (b) 2nd order equation (c) Langmuir adsorption isotherm (d) Freundlich adsorption isotherm*

3.8. Experiments of copper adsorption with actual industrial effluent

Result obtained from the experiments with synthetic solution in batch was validated with experimental data obtained with actual industrial effluent. Similar to the batch experiments with synthetic solution, 50 mL of industrial effluent containing copper of 100 and 300 ppm was contacted with 0.2 g Datura root powder for 15 min at pH 4. Result indicated that 90% adsorption in case of 100 ppm copper in aqueous feed of actual industrial effluent, while 55% adsorption for 300 ppm copper in actual industrial effluent. These results get validated with experiments performed by synthetic solution which is shown in Figure 8. Copper eluted from loaded Datura root powder was in same concentration compared to adsorbed copper.

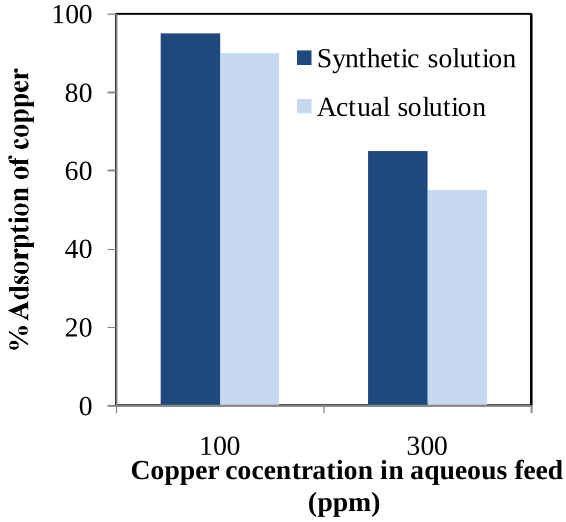

Figure 8. Comparison between synthetic copper solution and actual industrial effluent containing copper (Adsorbent: Datura root powder: 0.2 g/ 50 mL feed solution; Contact time: 15 min;Initial pH: 4)

3.9. FT-IR studies

FT-IR spectrum of Datura root powder adsorbent before loading and after loading of copper were documented to know about the functional group present on Datura root powder which is responsible for binding of copper ions in adsorption process. Alteration in vibrational frequency was used to predict the same [6]. FT-IR spectrum plot for Datura root powder is indicated in Figure 9. Comparative study for before and after copper adsorption was done by superimposing FT-IR spectrum of Datura root powder adsorbent before and after copper loading. FTIR spectrum indicates that strong band at 3434 cm^{-1}act for C-H, N-H and O-H stretching vibration due to presence of amino acids. Stretching bands at 2918, 2921 and 2928 cm^{-1} represents vibration of $–CH_3$ and $–CH_2$ groups. While, 553–633 cm^{-1} represents C-O-O and P-O-C bending of aromatic compounds (phosphates) represents drastic change in vibration in fresh and loaded adsorbent [14]. At 677.2 cm^{-1} showed the S-O bend [15]. It indicates that phosphate group from aromatic compounds are involve in copper adsorption process on Datura root powder.

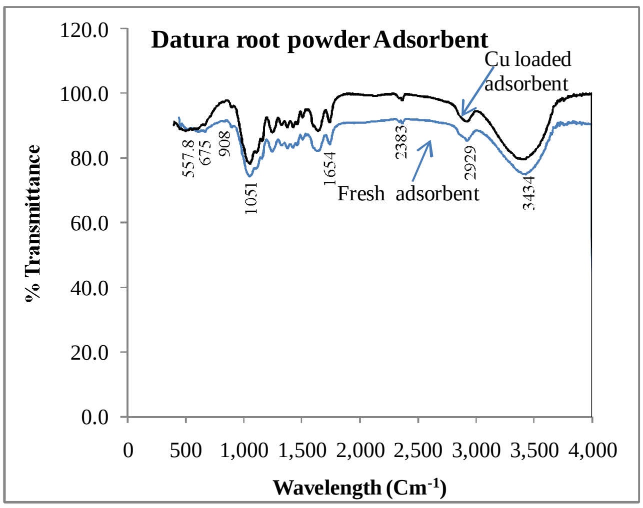

Figure 9. FT-IR of Datura root powder adsorbent (a) Fresh adsorbent (b) Cu loaded adsorbent

4. CONCLUSIONS

Laboratory scale experiment for copper adsorption using Datura root powder adsorbent was carried out using 4 g/L of adsorbent in 15 min contact time at pH 4 for maximum adsorption. 95% of copper found to be adsorbed from the sulfate solution containing 100 ppm copper. Adsorption of copper studied in different contacts in bench scale showed the copper loading capacity 947 mg/g of adsorbent. Batch scale experimental outcome fits well in pseudo second order rate reaction and follows Freundlich adsorption isotherm indicates multilayer adsorption process of copper ions on Datura root powder. Copper could be eluted from loaded adsorbent by using 10% sulfuric acid kept in contact for 60 min. The raffinate obtained after adsorption of copper could be disposed off safely without affecting environment and eluted copper could be further utilized for different purpose. FT-IR data indicates that aromatic (phosphate) group of Datura root powder participated in adsorption was located in the 557-675 cm^{-1} region of the adsorbent. This result indicates potentiality of Datura plant root powder as an adsorbent which is cost efficient, easily available. It provides copper adsorption process from electronic industrial effluents having potential to get commercialized after large scale studies. It will also give futuristic research direction to improve the existing process of effluent treatment.

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REFERENCES

[1] E. I. Ugwu & J. C. Agunwamba: A review on the applicability of activated carbon derived from plant biomass in adsorption of chromium, copper,and zinc from industrial wastewater. Environ Monit Assess 192, 240, 2020

[2] A. Gupta, V. Sharma, K. Sharma, V. Kumar, S. Choudhary, P. Mankotia, B. Kumar, H. Mishra, A. Moulick, A. Ekielski, P. K. Mishra: A review of adsorbents for heavy metal decontamination: growing approach to wastewater treatment. Materials 14, 4702, 1-45, 2021

[3] R. K. Gautam, A. Mudhoo, G. Lofrano, M.C.Chattopadhyaya: Biomass-derived biosorbents for metal ions sequestration: Adsorbent 3 modification and activation methods and adsorbent regeneration. J. Environ. Chem. Eng 244, 1–21, 2014

[4] B. B. Mathew, M. Jaishankar,V. G. Biju & K. N. Beeregowda: Role of bioadsoirbent in reducing toxic metals. J. Toxicol 2016, 4369604, 2016

[5] S. A. Begum, T. Yadamari, K. Yakkala, R. N. Gurijala:Adsorption and equilibrium studies of cadmium(II), chromium(VI) and lead(II) ions using ecofriendly biosorbent. Int. J. Eng. Res. Technol.4, 05, 696-702, 2015

[6] S. Kumar, T. Shahnaz, N. Selvaraju & P. V. Rajaraman: Kinetic and thermodynamic studies on biosorption of Cr(VI) on raw and chemically modified Datura stramonium fruit. Environ. Monit. Assess.192, 248, 2020

[7] V. Vinodhini, N. Das: Biowaste materials as sorbents to remove chromium from aqueous environment-comparative study. J. Agri. Bio. Sci. 4, 6, 19-23, 2009

[8] L. Hevira, E. Munaf, R. Zein: The use of Terminalia catappa L. fruit shell as biosorbent for the removal of Pb(II), Cd(II) and Cu(II) ion in liquid waste. J. Chem Pharm. Res. 7, 10, 79-89, 2015.

[9] J. Bayuo, K. B. Pelig-Ba, M. A. Abukar: Adsorptive removal of chromium(VI) from aqueous solution unto groundnut shell. Appl. Water Sci. 9,107, 2019

[10] R. Dubey, J. Bajpai, A. K. Bajpai: Chitosan-alginate nanoparticles (CANPs) as potential nanosorbent for removal of Hg(II) ions. Environ Nanotechnol, Monit Manag 6, 32–44, 2016

[11] A. K. Bhattacharya, S. N. Mandel, S. K. Das: Adsorption of Zn(II) from aqueous solution by using different adsorbents. Chem. Eng. J., 123, 43–51, 2006

[12] N. V. Nguyen, J. C. Lee, S. K. Kim, M. K. Jha, K. S. Chung, J. Jeong: Adsorption of gold(III) from waste rinse water of semiconductor manufacturing industries using Amberlite XAD-7HP resin. Gold Bull, 43 3, 200-207, 2010

[13] A. Kumari, S. Singh, K. Parmar, D. D. Pathak, M. K. Jha: Treatment of monazite processed effluent to recover rare earth metals (REMs). J. Ind. Eng. Chem., 83, 421-429, 2020.

[14] N. Ramamurthy, S. Kannan: Fourier Transform Infrared Spectroscopic analysis of a plant (calotropis gigantea linn) from an industrial village, Cuddalore Dt, Tamilnadu, India, Romanian J. Biophys. 17, 4, 269–276, 2007

[15] M. K. Jha, N. V. Nguyen, J. C. Lee, J. Jeong, J. M. Yoo: Adsorption of copper from the sulphate solution of low copper contents using the cationic resin Amberlite IR 120. J. Hazard. Mater. 08, 948-953, 2008