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Research Article

Biosorption of Cu (II) Ions from Contaminated Waste Water Using the Waste Leaves of Burans

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ABSTRACT
The conventional methods i.e. chemical precipitation, membrane filtration, ion exchange, carbon adsorption, electrowinning, phytoremediation etc used for the removal of heavy metals from water and waste waters are suffering with low performance, sludge generation, high cost and poor reliability. In the present study, we have used the waste leaves of Rhododendron arboreum as a low cost biosorbent for the removal of Cu (II) ions from waste water. The biosorption process is carried out under batch system. The batch system included contact time, pH, concentration, temperature and dosage. The maximum biosorption 38.98, 49.72, 71.10, 39.90 and 37.86 % was taking place at optimized conditions such as higher dose of biosorbent, contact time 60 minutes, higher pH , moderate temperature and lower concentration of metal ions. The equilibrium data of biosorption have been tested with different isotherm models i.e. Langmuir, Freundlich and Temkin isotherm models. High regression values and other parameters indicate the favourable adsorption of copper onto the Burans leaf powder. The Freundlich isotherm model is more favourable than Langmuir and Temkin isotherm models.

KEYWORDS: Removal processes; biosorption; batch system; optimized conditions; isotherms

INTRODUCTION

The term "heavy metals" is usually concerned with their toxic behaviour to environment and living organisms including humans [1]. The anthropogenic activities like mining, industrial, fossil fuel burning, metal finishing and extractions, alloying etc are exposed heavy metals into environment [1-4]. The conventional methods i.e. membrane filtration, precipitation, reverse osmosis, adsorption related to making carbon adsorbents, electrowinning, phytoremediation are poor efficiency, high cost, waste generation or taking long time to remove metals ions from water, waste water or soils. The biosorption process is universally accepted and follows all basic principles of green chemistry. Biosorption process is low cost, not harmful waste generated, highly efficient and can apply in large scale operations [5]. Some readily available waste biomaterials can reduce some more investment of cost. The exposure of copper in the environment is due to chemical rock weathering, bubble bursting, animal manure, aerosols, fossil fuel burning and nuclear plants. Copper helps in the process of blood formation and iron utilization but hyper accumulation of copper in human body causes lever damage, chronic poisoning and gastrointestinal catarrah [7-12]. The plant Burans is scientifically known as *Rhododendron arboretum*. This is a common gymnospermic plant found in the high altitude of Uttarakhand, Himanchal Pradesh and the North East states of India. It bears red colored flowers that are medicinally important.

MATERIAL AND METHODS

Preparation of biosorbent

The waste leaves of the plant (*Rhododendron arboreum*) were collected from the high altitudes of Kumaun hills, India. After collection of waste leaves, the leaves were washed 2-3 times with deionised water and then dried in the laboratory for three days. The moisture content of the leaves was removed by drying of leaves in a tray dryer under controlled conditions. Now the leaves grinded into particle size 120 microns and preserved in the sealed bottles.

Synthetic waste water

The synthetic waste water containing 1000 mg/L of copper ions was prepared by dissolving $CuSO_4.7H_2O$ (AR grade) in double distilled water. The pH of waste water wsa balanced 4 using digital pH meters and 0.1 N HCl and the this stock solution preserved in a plastic reagent bottle for making all applicable working solutions. Other working solutions having concentrations 10 to 50 mg/L copper ions and pH 1to 6 have been prepared from the stock solution by dilution and using 0.1 N NaOH or 0.1 N HCl solutions.

Biosorption study

The biosorption study was carried out by applying batch operations including contact time, pH variation, concentrations, temperature and dosage. In general, a desired amount of biosorbent was treated with the working solution containing copper (II) ions at a constant shake 170 rpm. After that, the leaf powder filtered out and the metal ion concentration was determined in the filtrate using Atomic Absorption Spectroscopy (AAS). The percentage removal of biosorption of metal ions is given as below:

$$\textbf{\% Biosorption} = (C_2 - C_1)\text{x}100/\ C_1$$

Where C_1 and C_2 are the initial and final concentrations of copper ions in waste water.

Effect of contact time

For contact time study, take 1 g of leaf powder and 100 ml of synthetic waste water containing 10 mg/L of Cu (II) ions in different Erlenmeyer flask used for the time periods 10 to 70 minutes at pH 4.

Effect of dosage and pH

The effect of dosage on the adsorption was done by using the dosage 0.1 to 1.0 g with 10 mg/L of working solution at pH 4. The influence of pH was studied by taking 1 g of biosorbents in six different Erlenmeyer flasks containing the solutions with pH 1 to 6.

Effect of concentration

The concentration dependency was carried out by the treatment of 1g of leaf powder with different solutions having concentrations 10 to 50 mg/L. Isotherms modelling in the adsorption study explain the distribution of adsorbate in two phases i.e. liquid and solid and the suitability of the process under batch operations. The equilibrium data of adsorption under concentration dependency has been checked by using Langmuir, Freundlich and Temkin isotherm models [3, 5, 19-20]. These isotherms will be discussed in the results and discussion section.

Effect of temperature

The temperature dependent study has been performed by the treatment of 1 g of biosorbent with the solutions containing 10 mg/L of Cu (II) ions in an incubated shaker at the temperatures 10 to 70^{0}C.

RESULTS AND DISCUSSION

The contact time is very important for the determination of minimum time required for the interaction of metal ion with biosorbents. It also helps in the explanation of kinetics of adsorption [13]. In the present study, minimum percentage biosorption is found 29.22 % after 10 minutes and it continuously increases till 50 minutes. After 50 minutes, it was observed 48.91 % and the maximum percentage removal is achieved 49.72 % after 60 minutes (Fig.1A). But after 60 minutes the removal becomes constant. It is due to the factor that the all active site or organic groups have been occupied by the copper ions (Fig.1A). The biosorption of Cu (II) ions from the waste water increases with the biosorbents dosage due to the maximum availability of active sites for the complexation of metal ions [14]. Minimum biosorption 10.69 % takes place at 0.1 g and gradually increases to 14.47 %. The efficiency of biosorption was found 31.74 % at 0.8 g of the amount of biosorbent. Maximum biosorption efficiency 38.07 % is achieved at the dosage 1.0 g after 25 minutes and at pH 4 (Fig. 1B). The percentage removal of Cu (II) ions was observed very less between the pH 1 and 3; but after that it increased to 37.19 % at pH 4. The maximum biosorption is found 71.10 % at pH 6 (Fig. 2A).At lower pH, all active or binding sites undergo protonation and become positively charged. Then repulsion occurs between the metal ions and active sites which results very low percentage of biosorption [15]. On other hand, about all the active sites are available for the complexation with metal ions because less probability of protolysis.

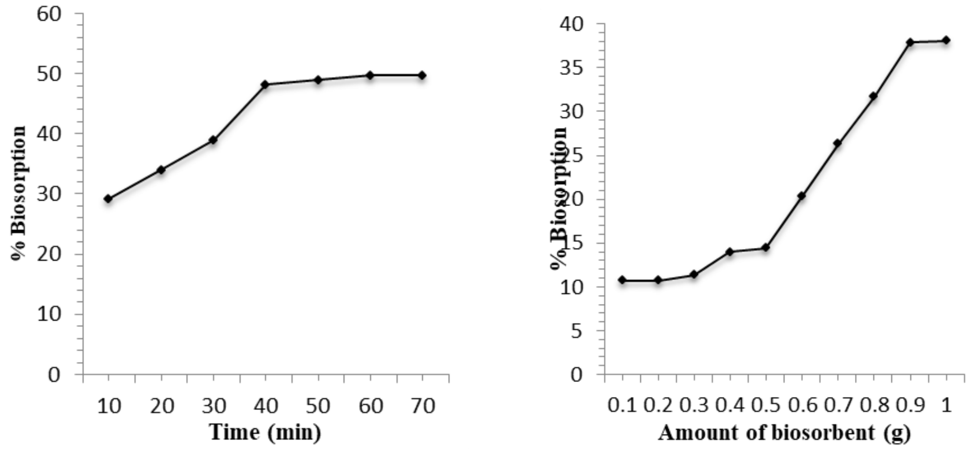

Fig. 1 (A): Effect of contact time (B) effect of dosage

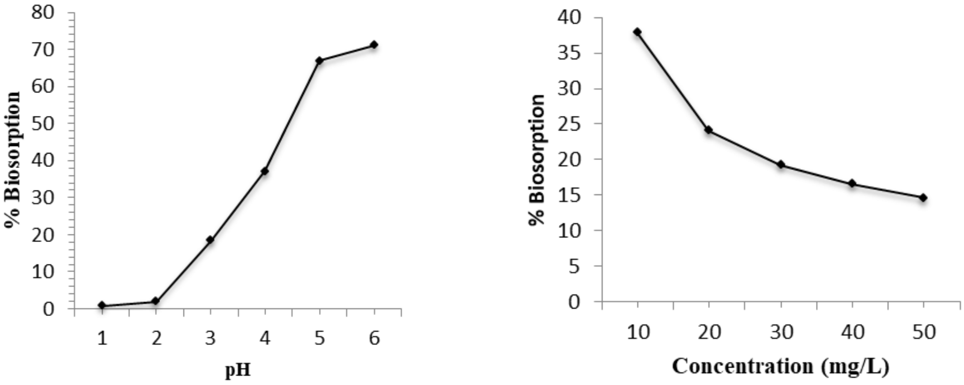

Fig. 2 (A): Effect of pH (B) effect of concentration

The percentage biosorption of Cu (II) ions onto the surface of biosorbent decreases with the increase in the concentration of Cu (II) ions in the working solutions. The maximum biosorption efficiency was found 37.86 % at 10 mg/L. Now, it decreased to 14.64 % at 50 mg/L but the amount of metal absorbed per gram of adsorbent was found 7.321 mg/g (Fig. 2B).The experimental data show that the percentage of biosorption decreases with the increase of concentration of the solutions but the amount of copper on the adsorbent increases. This may be attributed to the motive power of concentration gradient as the initial metal ion concentration [16-18]. The biosorption of metal ions is usually increased with the increase of temperature. The applying temperature range in batch operation is 10 to 70^{0}C at contact time 25 minutes and rpm 170 (Fig. 3). Minimum removal of copper takes place at 10^{0}C i.e. 33.49 % and increases very sharply to 39.00 % at 50^{0}C. At 60^{0}C, the maximum adsorption of copper (II) ions is recorded 39.90 % and reduces to 39.80% at 70^{0}C. The decrease of biosorption after certain temperatures may due to the dissolution of metal ions from the biosorbent into the solution [5,10-12].

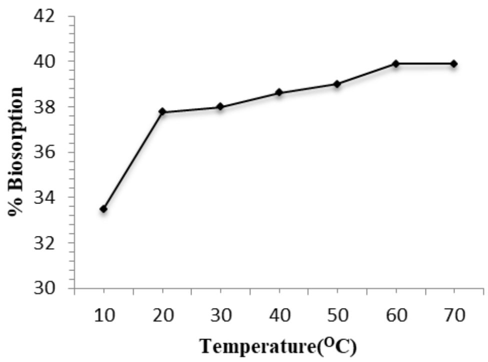

Fig. 3 Effect of temperature on the removal of Cu^{++} ions

The validation of equilibrium data of adsorption have been checked by developing different isotherm models. The suitability of equilibrium data of Cu (II) ions onto burans leaves were checked by Langmuir, Freundlich and Temkin isotherm models and their parameters evaluated [5]. The Langmuir isotherm model explains the monolayer adsorption on to the surface of leaf powder containing a definite number of active sites and these are arranged homogeneously [19]. Mathematically, the Langmuir isotherm can be represented by following equation:

$$C_2/q_e = 1/K_La + 1/K_LC_2$$

Where C_2 and q_e are the equilibrium concentration of copper containing solution and amount of copper adsorbate on the surface of burans leaf powder (mg/g). The constant K_L and a are the specific biosorption capacity (mg/g) and Langmuir biosorption equilibrium constant (L/mg). The values of K_L and a are found 8.928 mg/g and 7.267 L/mg from the graph C_2/q_e vs C_2. The important dimensional parameter of Langmuir isotherm is R_L, which can be defined mathematically as:

$$RL=1/1+aC1$$

Where a and C_1 are related to the Langmuir constant and the initial metal ion concentration (mg/L).The value of RL determines the representing isotherm to be either favorable (0<RL<1), unfavorable (RL>1), linear (RL=1) or irreversible (RL=0). The value of RL was observed <1 in all cases of batch system applied in for the concentration studies indicated favourable adsorption (Table 1). The regression value (R^2) is found 0.979 and that indicates the suitability of copper biosorption on to the leaf powder (Fig. 4).

Table 1: Value of RL

Initial metal ion concentration (C_0), mg/l	R_L
10	0.0135
20	0.0068
30	0.0045
40	0.0034
50	0.0027

The Freundlich isotherm model explains the different functional groups are varying with the energies on the heterogeneous surface of biosorbents [20]. The Freundlich model is mathematically written as:

$$\log q_e = \log K_F + 1/n \log C_2$$

Where q_e and C_2 are the amount of Cu^{++} ions adsorbed on the surface of leaf powder (mg/g) and the equilibrium concentration of Cu^{++} ions in the solution (mg/L). The constants K_F and n are the adsorption capacity and intensity of biosorption. The values of K_F and 1/n have been calculated from the slope and intercept of the graph log q_e versus log C_2 (Fig. 5). The values of K_F and 1/n are found 0.294 mg/g and 0.343. The value of 1/n should be less than 1 for the favourable adsorption and that found less than one in the present study. A high regression (R^2 = 0.988) value indicates the equilibrium data of adsorption are best fitted to Freundlich isotherm model (Fig. 5).

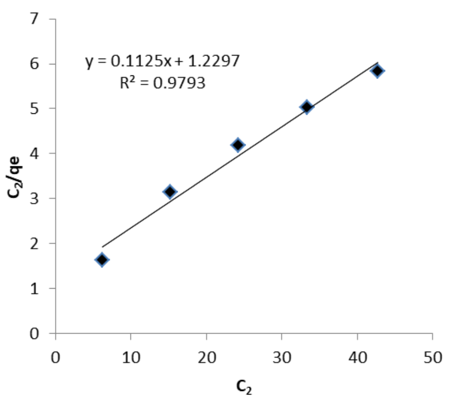

Fig. 4: Langmuir isotherm model

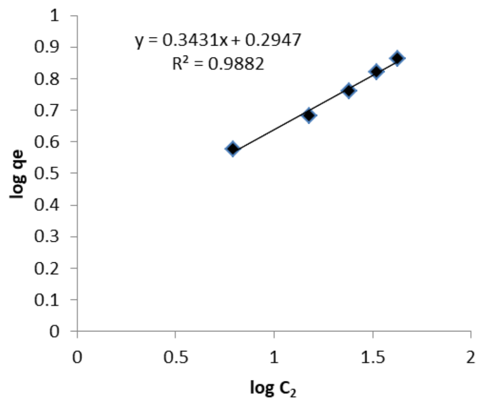

Fig. 5: Freundlich isotherm model

Temkin isotherm model explain the meta-metal ions interaction adsorbed on the leaf powder and a linear decrease of heat of biosorption for all adsorbate metal ions [3]. The Temkin isotherm model is mathematically written as:

$$q_e = X + Y \ln C_2$$

Where C_2 is the equilibrium concentration of metal ions in mg/L, q_e is the amount of adsorbate in mg/g, X is related to adsorption capacity and Y is the Temkin constant. The values of X and Y have been found 1.611 and 1.401 (Table 2).

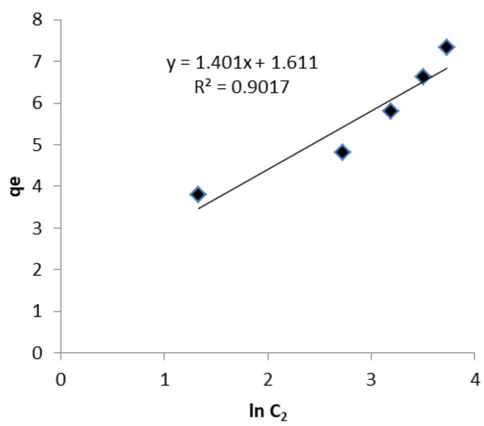

Fig. 6: Temkin isotherm model

Table 2: Parameters of Isotherms model

Isotherm	Parameters	Calculated values
Langmuir isotherm model	K_L (mg/g)	8.928
	a(L/mg)	7.267
	R^2	0.979
Freundlich isotherm model	K_F (mg/g)	0.294
	1/n	0.343
	R^2	0.988
Temkin isotherm model	X(mg/g)	1.611
	Y	1.401
	R^2	0.901

CONCLUSION

The conventional techniques used for the removal of heavy metals are waste generating, high cost and not efficient. Biosorption is relatively new and that is related to sustainability. It fulfils all the basic principles of green chemistry. In the present study, we have achieved the optimized conditions for the removal of copper ions from the waste waters. The maximum removal efficiency has been observed at contact time 60 minutes, 1 g dosage of leaf powder, low metal concentrations, pH 6 and moderate temperatures. Applying these conditions, we can remove copper from waste waters in large scales from waste waters using waste leaves of *Rhododendron arboreum*.

CONFLICT OF INTEREST

The authors declare no conflict of interest in this research article.

REFERENCES

1. Ahmed I, Iqbal HMN, Dhama K. Enzyme-based biodegradation of hazardous pollutants-An overview. J Exp Biol Agric Sci 2017; 5: 402-411.
2. Joshi NC. Biosorption: A green approach for heavy metal removal from water and waste waters. RJLBPCS 2108; 4: 59.
3. Joshi NC. A brief discussion on biosorption and biosorption technology. J Pharm Chem Biol Sci 2018; 5: 330-336.
4. Ullah S, Zuberi A, Alagawany M, Farag MR, Dadar M, Karthik K, Tiwari R, Dhama K, Iqbal HMN. Cypermethrin induced toxicities in fish and adverse health outcomes: Its prevention and control measure adaptation. J Environ Manag 2018; 206: 863–871.
5. Joshi NC and Bahuguna V. Biosorption of copper (II) on to the waste leaves of kafal (myrica esculenta). Rasayan J Chem 2018; 11: 142-150.
6. Joshi NC, Chhibber VK. A kinetic and thermodynamic study of copper removal using deodar leaves. J Chem Chem Sci 2017;7: 280-288.
7. Nolan K. Copper toxicity syndrome. J Ortho Psychiatry 2003; 12: 270-282.
8. Vasu EV. Adsorption of Ni (II), Cu(II) and Fe(III) from aqueous solutions using activated carbon. E J Chemistry 2008; 5: 1-9.
9. Joshi NC, Sharma R, Singh A. Biosorption: A review on heavy metal toxicity and advances of biosorption on conventional methods. J Chem Chem Sci 2017; 7: 714-724.
10. Joshi NC, Bhandari NS, Kumar S. Biosorption of copper (II), iron (II) and Zn (II) from synthetic waste water using banjh leaves as low cost adsorbent. Env Sci Indian J. 2011; 6: 148-153.
11. Bhandari NS, Joshi NC, Shah GC. Study of Cu, Fe and Zn removal using key lime leaves (*Citrus aurentifolia*) as low cost adsorbent. J Indian Chem Soc 2012; 89: 383-387.
12. Bhandari NS, Joshi NC, Kumar S. Sorption studies of Cu (II), Fe (II) and Zn (II) onto deodar leaves (*Cedrus deodara*). Env Sci Indian J. 2011; 6: 75-79.
13. Awwad AM, Salem NM. Biosorption of copper(II) and lead(II) ions from aqueous solutions by modified loquat (Eriobotrya japonica) leaves (MLL). J Chem Eng Mater Sci 2013; 3: 7-17.
14. Tichaona N et.al. Isotherm study of the biosorption of Cu (II) from aqueous solution by Vigna Subterranea (L.) Verdc Hull. International J Sci Tech Res 2013; 2: 199-206.
15. Sciban M, Klasnja M. Study of the adsorption of copper (ii) ions from water onto wood sawdust, pulp and lignin. Ads Sci Tec 2004; 22: 195-206.
16. Zacharia K, Jackson K. Biosorption studies of lead and copper using rogers mushroom biomass 'Lepiota hystrix'. South African J Chem Eng 2017; 23: 62-70.
17. Ahalya N, Ramachendra T. Restoration of wetlands feasibility aspects of biological restoration. In: Presented at the National Conference on Aquatic Restoration and Biodiversity, on 15the16th Feb. Coimbatore, India: Kongunadu Arts and Science College; 2002.
18. Wael M, Ibrahim, Asad F, Hassan, Yahia A, Azab. Biosorption of toxic heavy metals from aqueous solution by Ulva lactuca activated carbon. Egyptian J Basic Appl Sci 2016; 3: 241-249.
19. Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. J Am Chem Soc 1918; 40: 1361-1403.
20. Freundlich HM F. Uber die adsorption in losungen. Zeitschrift fur Physikalische Chemie (Leipzig) 1906; 57A: 385-470.

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