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REMOVAL OF COPPER (II) FROM AQUEOUS SOLUTION USING CHEMICALLY ACTIVATED BANANA PEELS AS AN ADSORBENT

VIKAL GUPTA[1], SHIVANGI DAVE[2] AND NEHA PARIHAR[2]

Department of Chemistry, J.N.V. University, Jodhpur 342 001, Rajasthan, India

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ABSTRACT

The use of chemically activated banana peels as an adsorbent for removal of copper ions from aqueous solution has been investigated. The dried banana peels were treated with 0.5 N HNO_3 solutions. Batch experiments have been conducted at different concentration to evaluate the maximum adsorption capacity of banana peels. The influence of pH, contact time, adsorbent dose and particle size was investigated at room temperature. The adsorption data were fully fitted with the Langmuir and Freundlich isotherm and followed a pseudo second order kinetic model. Adsorption is exothermic and spontaneous according to thermodynamic study. This study shows that chemically activated banana peels can be used as effective adsorbent because it has great potential to remove the copper ion. Optimum removal for Cu^{+2} was observed at a pH of 5.

KEY WORDS : Banana peels, Isothermal model, Biosorption, Heavy metals.

INTRODUCTION

Water pollution is developed due to increase of heavy metals through the discharge of industrial effluents. Massive urbanization has been continuously releasing waste and waste water for last ten years to the ecosystem. It causes toxicity to living being. Recently metal production has decreased in some countries due to strict legislation, improved cleaning or purification technology and altered industrial activities.

The heavy metals contain high level of toxicity and produce major problems for human health. So removal of heavy metals is more important for the environmental concern. Copper is the major available type of heavy metals for human and aquatic environment life. Copper in the blood system may generate reactive free oxygen species and damage the protein, lipids and DNA. At high concentration copper shows potentially toxicity. Excess Copper compound in the body may affects on aging, schizophrenia, mental illness and Indian childhood cirrhosis. Copper has damaged the marine ecosystems and it is also responsible for damage of the liver, kidneys and the nervous system.

Various methods are used for the removal of heavy metals from aqueous solution such as chemical precipitation, ion exchange, ultra filtration, osmosis and adsorption but these methods have some limitations like production of secondary wastes, large quantity of slug formation and high operational costs. But adsorption is a better method than the other methods because of its simple operation design, sludge free environment, low cost and ecofriendly nature (ElNemr, 2007; Ibrahim *et al*., 2006).

The high cost of activated carbon and other conventional adsorbents motivates the researchers to use low cost agricultural products and by products as adsorbents for the removal of heavy metals.

Several types of agricultural waste materials such as rice husk, sugarcane bagasse, saw dust, brazil nutshell, grape stack, mango peels, coconut shell and banana peel and related materials had shown better results when used as adsorbents for heavy metals in comparison with those of other physical and chemical techniques (Ibrahim *et al*., 2006; Abiedeen *et al*., 2013).

Banana is one of the major important crop of fruit which has grown worldwide in huge quantity in more than 130 countries like Brazil, China, Columbia, Cameroon, Ecuador, Ghana, India and Indonesia. The worldwide production of banana was 139.2 million tons in year 2012 while the total production of banana in india was about 24.9 million tons at the same year. Banana peels are produced as waste in large quantity in house hold garbage.

Banana peels have many constitutes such as cellulose, hemicelluloses, lignin and pectin in its biomass which contain carboxyl, hydroxyl and amine types of functional groups which is important for binding of metal ions on Biosorbent (Annadurai *et al.,* 2003). Banana peels have higher maximum adsorption capacity for heavy metals. The main aim of this research is to estimate the adsorption capacity of activated banana peels as Biosorbent. The effects of various parameters like pH, adsorbent dose, contact time, particle size and metal ion concentration have also be analysed.

MATERIALS AND METHODS

Preparation of adsorbent: Banana peels were selected from local fruit market of Jodhpur, (Rajasthan). The collected peels were then washed with distilled water for several times to remove dust, ash and other contaminants. The washed materials were dried in sunlight for 2-3 days. After 3 days these peals were crushed into small pieces and again washed with distilled water and dried in a hot oven for 3 hrs at 75 ^oC.

The dried banana peels were activated by treating with 0.05 M nitric acid solution for 3 hrs and also keeping it in air oven for 10 hrs at 60 ^oC. The activated banana peels (ABP) were washed thoroughly with distilled water to remove free acid and dried in the oven for 40 hrs at 60 ^oC.

Preparation of stock solution

The stock solution of copper (II) containing 1000 mg/L was prepared by dissolving 3.929 g of copper sulphate in one liter double distilled water. This solution was diluted as required to obtain standard solution containing 10-200 mgL^{-1} of Cu (II).

Adsorption experiment

The powdered material of activated banana peels was added to 100 mL of metal ion solution with intial concentration varying from 10 mg/L to 200 mg/L into 250 mL conical flasks separately. Each solution was shaked thoroughly using orbit shaker rotating with 250 rpm speed. After the completion of every set of experiments, the residual was separated by filtration using Whatman filter paper no. 42. The concentration of Cu(II) ion in filtrate was directly measured by AAS after finishing of filtration process. pH of each and every solution was adjusted by adding 0.1 M NaOH and 0.1 M HCl drop by drop. The whole experiment was carried out at room temperature.

The percent removal (%) of copper was calculated by using following equation

$$\text{Adsorption (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad ..(1)$$

Where C_0 is initial metal ions concentration in solution and C_e is equilibrium metal ion concentration in solution.

Adsorption isotherms

The adsorption isotherms describe the equilibrium relationship between the adsorbed metal ions onto the adsorbents. Langmuir and Freundlich adsorption isotherm models were used to describe the interaction of Cu(II) ions with adsorbent like activated banana peels.

(i)Langmuir adsorption isotherm

This model suggests that an adsorption occurs on the surface by monolayer or homogenous surface without interaction between the adsorbed molecules. Here monolayer or homogenous surface contain finite number of adsorption sites. According to Langmuir theory, the linear form of adsorption isotherm can be represented as

$$q_e = \frac{q_{max}\, bC_e}{1 + bC_e} \quad ..(2)$$

The above equation can be rearranged as

$$\frac{1}{q_e} = \frac{1}{bq_{max}C_e} + \frac{1}{q_{max}} \quad ..(3)$$

where C_e is equilibrium concentration of ascorbate (mg g^{-1}), q_e is amount of metal ion adsorbed (mg g^{-1}), q_{max} is monolayer adsorption capacity (mg L^{-1}) and b is Langmuir constant related to free adsorption energy (mg^{-1}).

A graph was plotted between C_e/q_e against C_e, which showed a straight line with intercept $1/q_{max}$ b and slope $1/q_{max}$ as represented in Figure 1. The adsorption isotherm constants were calculated from the linear regression of the experimental data and shown in Table 2.

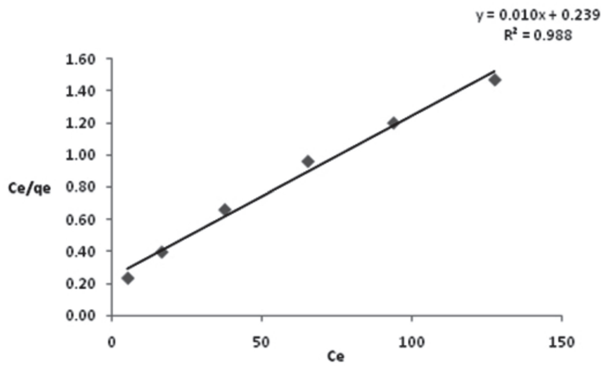

Fig. 1. Langmuir adsorption isotherm for copper adsorption onto ABP

(ii) Freundlich adsorption isotherm

This model deals with adsorption onto heterogeneous surface with involving multilayer adsorption. Here adsorption increases with increasing concentration.

The linear form of Freundlich adsorption isotherm can be given by following equation

$\log q_e = \log K_f + 1/n \log C_e$

Where K_f is constant, indicative of adsorption capacity and constant 1/n shows the intensity of adsorption. The linear plot of Freundlich equation for copper adsorption and the calculated parameters are shown in Fig. 2 and Table 2 respectively. The Freundlich isotherm model was found best fitted with experimental data due to higher value of R^2.

RESULTS AND DISCUSSION

Effect of pH on removal of Cu(II)

The pH of solution is one of the most important factor for metal adsorption process from aqueous solution. The effect of pH on adsorption of copper on to Activated Banana peels (ABP) was studied in a range of 2-6 as shown in Fig. 3. The maximum removal of metal ion was found to be 74% at pH 5. At higher pH; the removal was low as compared to optimum condition. This can be explained as the binding site may not be activated in basic condition. On higher pH, the copper is started precipitating as $[Cu(OH)_2]$ by which the removal is not completely by adsorption.

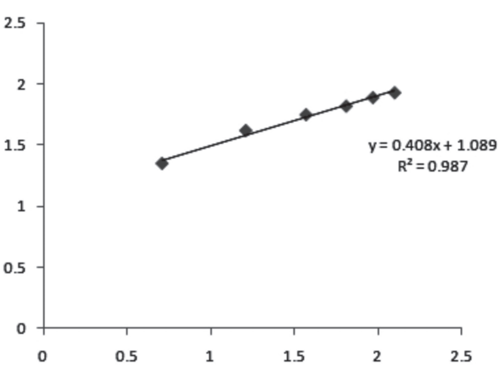

Fig. 2. Freundlich adsorption isotherm for copper adsorption onto ABP.

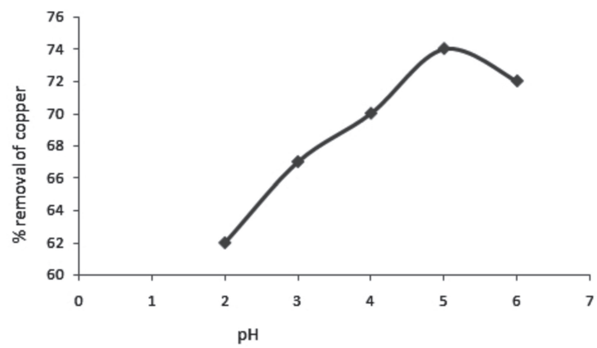

Fig. 3. Effect of pH on the removal efficiency of ABP.

Effect of adsorbent dose on removal of Cu(II)

The effect of adsorbent dose was investigated with change in biomass dosages of activated banana peels powder from 3-15 g L^{-1} and maintaining other variables as constant, i.e. particle size of biomass, metal ion concentration, contact time and pH.

As shown in Fig. 4, with the increase in biomass of adsorbent, the removal efficiency is also increased. This increase is due to the availability of more active sites for the uptake of metal ions at higher adsorbent dose. This adsorption of Cu(II) is not affected by further increasing the adsorbent amount due to available metal ions are already adsorbed by the adsorbent.

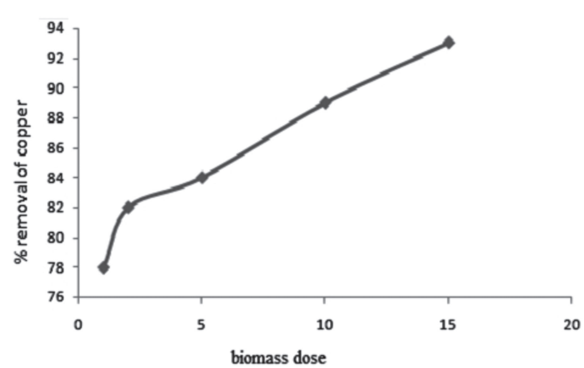

Fig. 4. Effect of biomass dosages on % removal of copper.

Effect of metal ion concentration on removal efficiency

The experiments were carried out with change in Cu(II) ion concentration from 25 to 175 mg L^{-1} and maintaining other parameters constant as shown in Table 1. By increasing the concentration of Cu (II) ion, the % adsorption increases initially as shown in Fig. 5 because initial concentration of metal ion provides an important driving force to overcome all the mass transfer resistance between the solution and solid phases. Thus a higher initial concentration of metal ion is responsible for increase in the adsorption capacity.

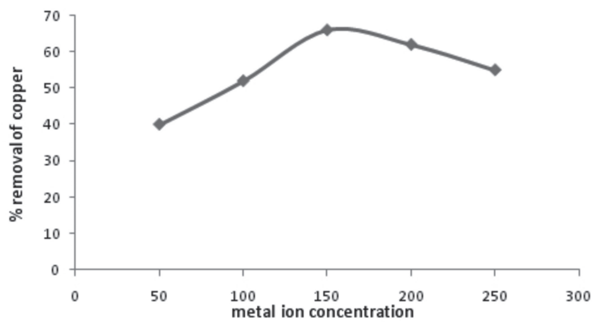

Fig. 5. Effect of metal ion concentration on % removal of copper

A decrease in removal efficiency at higher metal concentration could be due to rapidly filled binding sites and saturation of adsorption sites on the surface of the adsorbent.

Effect of contact time on removal of Cu(II)

Experiment for contact time was carried out from 20 to 80 minutes and other parameters were kept constant. Fig. 6 shows the effect of contact time on adsorption of copper metal ion by ABP. The adsorption rate increases with contact time because initially the availability of the large number of vacant active binding sites on the surface of ABP and the metal ion rapidly diffuses from the bulk of the solution to the adsorbent surface. However further increase in contact time up to 2 hrs brings no significant change in Cu(II) removal. Because after some time number of vacant binding sites are very short and these sites are difficult to be occupied Cu^{+2} ions due to formation of repulsive forces between copper ion on the solid surface and the liquid phase. Thus 1 hr was selected as optimum time for the removal of metal ion.

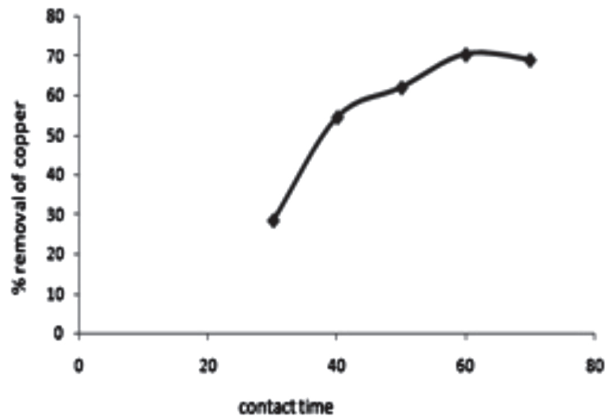

Fig. 6. Effect of contact time on % removal of Cu(II) ions.

Effect of particle size on removal of Cu(II) ion

The experiment was conducted with change in particle size of activated banana peels powder from 50-350μm and maintaining other parameters as constant. The Fig. 7 shows that removal efficiency of ABP is increased with decrease in particle size. It is due to increase in surface area with the decrease in particle size.

Table 2. Langmuir and Freunlich isotherm parameters

Isotherm	Parameters	Cu(II)
Freundlich isotherm	m	0.408
	K_f(mg g^{-1})	12.274
	R^2	0.987
Langmuir isotherm	q_{max}(mg g^{-1})	10.0
	R^2	0.988
	b(L mg^{-1})	0.04

Fig. 7. Effect of particle size on% removal of copper

Table 1. Experimental Conditions

Experimental Conditions	M_s(g L^{-1})	pH	P_s(μ m)	T(min)	C_o(mg L^{-1}
Effect of adsorbent dosages M_s (g L^{-1})	**3-15**	5	250	60	100
Effect of pH	8	**2-6**	250	60	100
Effect of particle size P_s (μm)	8	5	**50-350**	60	100
Effect of contact time T(min)	8	5	250	**20-80**	100
Effect of concentration of Cu(II) ion C_o (mg L^{-1})	8	5	250	60	**25-175**

CONCLUSION

Peel of banana is an effective adsorbent and also less expensive for the removal of Cu(II) ions from aqueous solution. The adsorption experimental data indicate that efficiency is dependent on operating variables such as pH, adsorbent dose, initial metal ion concentration and contact time. The optimum pH range for removal of copper is found to be 2-5. Here rate of adsorption increases with increasing adsorbent dose and decreases with increasing metal ion concentration. The adsorption capacity of activated banana peels is much better than other agricultural adsorbents. This study concludes that the low cost activated banana peels can be used as an alternative to expensive activated carbon for removal of Cu(II) metal ion. The adsorption data is fully fitted with Langmuir isotherm model and data also follows pseudo second order kinetic model.

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