BIOREMEDIATION OF COPPER (II) FROM AQUEOUS SOLUTION USING TAMARIND KERNEL POWDER

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ABSTRACT

Heavy metal pollution is nowadays one of the most important environmental concerns. Anthropogenic activities like metalliferous mining and smelting, agriculture, waste disposal or industry discharge a variety of metals such as Ag, As, Au, Cd, Co, Cr, Cu, Hg, Ni, Pb, Pd, Pt, Rd, Sn, Th, U and Zn, which can produce harmful effects on human health when they are taken up in amounts that cannot be processed by the organism. Physical and chemical methods have been proposed for the removal of these pollutants. Conventional methods to remediate heavy metals contaminated site are excavation and solidification/ stabilization, these technologies are suitable to control contamination but not permanently remove heavy metals. Nevertheless, they have some disadvantages, among them cost-effectiveness limitations, generation of hazardous by-products or inefficiency. Biological methods solve these drawbacks since they are easy to operate, do not produce secondary pollution. Heavy metals having relatively high density are toxic at low concentration. Microorganisms and plant are usually used for the removal of heavy metals. Bioremediation is increasingly considered for clean-up of metal contaminated and polluted ecosystem. All the metals are toxic, but some of these are useful in low concentration. These large verity of heavy metals cause serious water pollution

KEY WORDS : Heavy metals, Bioremediation, Bio adsorption , Tamarind kernel powder

INTRODUCTION

1.A large variety of inorganic chemicals find their way into normal water from municipal and industrial waste water urban run offs. Then the pollutants, comprising of compounds of Hg, Pb, As, Cd, Na, Ca, F, Cu, Cr etc. injure or kill fish and other aquatic life and also render the water unfit for drinking. Heavy metals are not biodegradable and tend to accumulate in living organism causing various diseases and disorders.

2.The normal growth and development of animals and human beings are brought about by specific enzymes present in their bodies. The toxic ions attack the active sites of these enzymes, react with the SH groups of the enzyme and thus cause their complete inactivation.

3. Removal of toxic heavy metal from industrial waste water has been practical for several decades. The conventional physico-chemical removal methods such as chemical

precipitation, electro plating ,membrane separation, evaporation or resin ion exchange, reduction, reverse osmosis, solvent extraction and adsorption. Most of the methods require high investment of capital and also expensive chemicals, making them unsuitable for treatment. The most widely used adsorbent for this purpose is activated carbon, but its overlying coast has lead to search for cheaper alternative materials. In recent years, several studies have been carried out for the removal of toxic metals by biosorption from the aqueous effluents using agricultural by products. Removal of heavy metals from aqueous solution by biosorption plays an important role in water.

4. The discovery and development of biosorption is the base of a new technology of heavy metal removal from dilute solution. The interesting features of the newly developed bioadsorbents are their high versatility, metal selectivity, high uptake, high tolerance for organics and regeneration. Different materials are used for this type of adsorption. Some of the examples are tamarind kernel powder, coffee waste powder, egg shell, paper thread , charcoal, prosopis cineraria leaf powder, Nicols plant material.

5. The aim of the present work is to use and abundantly available tamarind kernel powder as an adsorbent for removal of the toxic heavy metals such as Cu(II)

MATERIALS AND METHODOLOGY

FREUNDLICHISOTHERM

Freundlich equation is an empirical equation based on the adsorption on a heterogeneous surface. qe = KfCe1/n Where, Ce = Equilibrium concentration of Cu(II) ion (mg/L) qe = Amount of Cu(II) ion bound to per gram of the adsorbent at equilibrium (mg/g). Kf,n = are Freundlich constants related to sorption capacity and sorption intensity of the sorbent respectively. The logarithamic linear form of the freundlich isotherm equation is

Log(x/m) = log k + 1/n log Ce

Where,

x/m = is the amount of Cu(II) adsorbed/unit wight of adsorbent TKP.

Ce => is the equilibrium concentration of Cu(II)

PROCEDURE FOR THE ESTIMATION OF Cu.

The 20ml of the filtrate pipetted out into a conical flask. Ammonium hydroxide is added drop by drop till a permanent precipitate is formed.The precipitate is redissolved by adding required quantity of acetic acid.About 15ml 5% solution of Solution of potassium iodide is added and liberated iodine is litrated against sodium thiosulphate solution. Starch is used as the indicator towards the end. Titration continued until the blue colour to fade. About 10 ml of 10% ammonium thiocyanate solution is added. Then titration continued until the blue colour is just discharged. The titration is repeated till concordant values are obtained. From the titre values, the normality of copper sulphate and the mass of copper in the whole of the given solution can be calculated; knowing that the equivalent mass of copper is 63.54. Calculation

Normality of dichromate =

$W \times 4/49.04 = N1$

20 ml of $K_2Cr_2O_7$ solutions=V1ml $Na_2S_2O_3$.

Then, $N_1V_1 = N \times 20$

$N_1 = N \times 20/V_1$

Volume of $CuSO_4$ Solution taken for each titrations =20 ml

Volume of thiosulphate used up =v2ml

Therefor, Strength of copper sulphate solution $N_2=N_1 \times v_2/20$

Mass of copper in the whole of the given solution $=N_2 \times 63.54/10=wg$

EFFECT OF CONTACT TIME

In order to determine the effect of contact time 5 g of adsorbent was stirred with 100ml of 0.1N cu(II) solution at different time intervals.The pH of the solution kept constant as 3.9.At the end of each time the solution was filtered rapidly and the Cu(II) ion content of the filtrate determined.The difference between the initial concentration (C_0) and final concentration(C_t)was used to calculate the percent removal of Cu(II) ion using equation $\%R=[(C_o-C_t)/C_o]100$. In batch equilibrium experiments the amount of Cu(II) adsorbed at equilibrium q_e (mg/g) was calculated using the equation.

$q_e=[(C_o-C_e)/m_a]v$

where,

'C_0' and 'C_e' are Cu(II) ion concentrations initially and at equilibrium respectively .'v' the volume of the solution(L) and 'm_a' is the adsorbent mass.

EFFECT OF ADSORBENT DOSE

The study of adsorbent concentration on adsorption of Cu(II) was carried out by taking 100 ml of 0.1 N $CuSO_4$ solution for contact time 30 minutes with adsorbent TKP. The pH of the solution kept constant as 3.9. TKP dose varied from 2-32g.The solution get filtered using filter paper into labeled conical flask. Amount of copper present in each 100ml is determined using iodometrically

EFFECT OF CONCENTRATION OF Cu(II) SOLUTION

The study was carried out by taking 5g of adsorbent TKP with varying concentration of cu(II) solution from 0.1 to 0.9 N for contact time 30minute. The titration was carried out as given in the procedure. From the titre value mass of Cu adsorbed was calculated.

EFFECT OF PH

The variation in the adsorption of Cu(II) by TKP as a function of pH was studied over pH range 1-12 using 100ml of 0.1N $CuSO_4$ solution with adsorbent concentration 5g/100ml. pH of the sample was adjusted by adding 0.1N HCl or NH_4OH . All experiments were conducted at room temperature. pH of the solution can be measured using digital pH meter.

ADSORPTION STUDIES ON BORDEAUX MIXTURE

The compounds and mixtures of sculpture and cu with lime have been used as fungicide is toxic to the parasite and not to the host. There are several formula for preparing

Bordeaux mixture 4:4:50 or 5:5:50. Standard Bordeaux mixtures are made experimentaly by dissolving 1kg of Cuso4 in 50 L water and 1kg of quicklime in 50 L water and mix the two by placing the solution in water bath. Dipped tip of polished knife in the mixture in order to test free copper.

RESULT AND DISCUSSION ADSORPTION OF Cu (II) AS A FUNCTION OF ADSORBENT DOSE

For this experiment different masses of adsorbent TKP were stirred with Cu(II) solution for 30 minutes. The results are presented in the table1.It is evident from the figure 1 that the adsorption increases with increasing amount of adsorbent. Increasing adsorption percentage is due to the increase in available number of binding sites, when the amount of adsorbent mass increases. It is shown in the figure that the percentage removal increases because of increased surface area owing to the increase in the total number of adsorption sites resulting in higher Cu(II) removal.

Table 1

Adsorbent dose(g)	Normality(N)of filtrate	Normality get adsorbed (N)	Mass of Cu(II) get adsorbed(g)
4	0.0895	0.0105	0.0667
6	0.084	0.0160	0.1017
8	0.078	0.022	0.1398
10	0.0735	0.0265	0.1684
12	0.072	0.028	0.1779
14	0.067	0.033	0.2092
16	0.0655	0.0345	0.2192
18	0.0625	0.0375	0.2383
20	0.0575	0.0425	0.2700
22	0.0562	0.0435	0.2764
24	0.05	0.048	0.3050
26	0.0445	0.0558	0.3546
28	0.036	0.064	0.4067
30	0.031	0.069	0.4385
32	0.031	0.07	0.4449

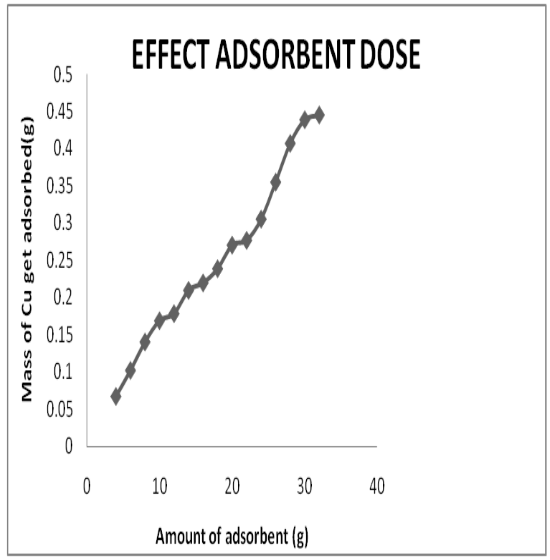


Chart 1

ADSORPTION OF Cu(II)AS A FUNCTION OF INTIAL CONCENTRATION OF Cu(II) SOLUTION

Cu(II)solution ,whose concentration ranging from 0.1N-0.9N were used in the experiment this corresponding to the concentration of the metal ion found in, effluents form related industries. Results are presented in the table-2 It is evident from the fig-2 that the amount of metal ion adsorbed get increases with concentration.

Table 2

Concentration Cu(II)solution (N)	Normality of filtrate (N)	Normality get adsorbed(N)	Weight of Cu get adsorbed (g)
0.1	0.096	0.004	0.0254
0.2	0.1665	0.0335	0.2129
0.3	0.256	0.044	0.27962
0.4	0.3275	0.0725	0.4602
0.5	0.3525	0.1475	0.9374
0.6	0.36	0.24	1.5252
0.7	0.387	0.313	1.989
0.8	0.394	0.406	2.580
0.9	0.3995	0.500	3.1775

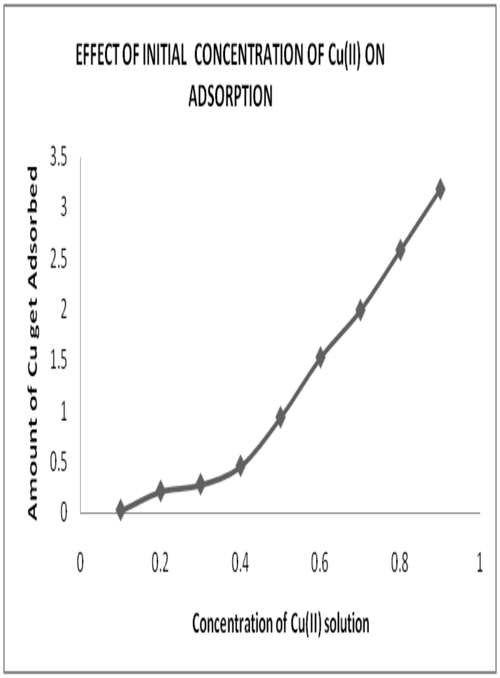


Chart 2

ADORPTION OF Cu(II)AS A FUNCTION OF PH

The effect of PH on the adsorption characteristics of TKP was determined in the PH range 1-12.The results represented in the table3.Studies indicate that the system is strong PH dependent. The results shown in the figure -3 indicate that the adsorption rate is lower in acidic range due to high positive charge density. The electrostatic repulsion resulting in lower rate of adsorption. With the increasing pH electrostatic repulsion decreases due to reduction of positive charge density on the sorption sites of adsorbent resulting in increasing in rate of adsorption.

PH affects degree of ionization and speciation of adsorbate species. It is evident from the figure that maximum removal of Cu(II)is obtained of PH range 4.5to5.9. At higher PH value a decrease in adsorption of Cu(II)was observed which may be due to the ionic repulsion between ionic sites of adsorbent surface and copper ions.

Table-3

p^H	Normality of Filtrate (N)	Normality of Cu get adsorbed(N)	Mass of Cu(II) get adsorbed(g)
1.15	0.092	0.008	0.05084
1.5	0.091	0.009	0.05719
3.9	0.0885	0.0115	0.07308
5.9	0.0221	0.07789	0.495
9.7	0.043	0.057	0.3362
11.6	0.0535	0.0465	0.2

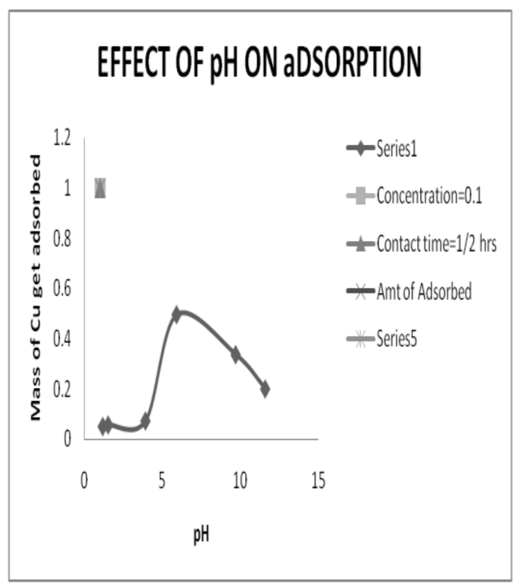


Chart 3

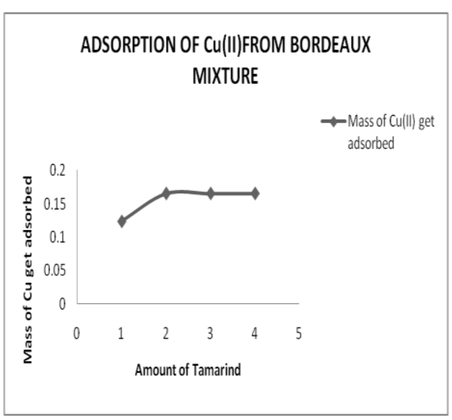
ADSORPTION OF Cu(II) IONS FROM BORDEAUX MIXTURE USING TKP

Bordeaux mixture consist of both Cu2+ and Ca2+ ions .The removal of Cu(II)by adsorption from Bordeaux mixture depends on pH,amount of adsorbent,contact time, temperature etc.Adsorption Cu(II)from the Bordeaux mixture was studied by changing the adsorbent dose. Normality of Cuso4 in the Bordeaux mixture using for the study is 0.0415 N .From the figure-4 it is clear that the amount of TKP required for the removal of Cu(II)from Bordeaux mixture is in the range 5-10.

Table-4

Amount of adsorbent(g)	Normality of filtrate(N)	Normality get adsorbed(N)	Mass of Cu(II) get adsorbed(g)
5	0.022	0.0195	0.1239
10	0.0155	0.026	0.16523
15	0.0155	0.026	0.16523
20	0.0155	0.026	0.16523

Chart 4



ADSORPTION ISOTHERM

The adsortion isotherm indicate how the adsorption molecule distributed between the liquid Phase and solid Phase when adsorption process reaches an equilibrium state .The quantification of the adsorption capacity of TKP for the removal of Cu(II)from the solution was studied using Freundlich and Langmuir isotherm.

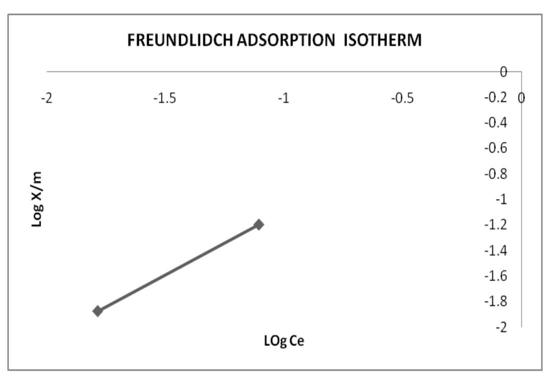
FREUNDLICH ISOTHERM

Log(x/m)= log k+(1/n) log Ce

Table 5

Amt of adsorbent(g)	Initial Concentration (Co)	Equilibrium concentrution (Ce)	X=(Co-Ce)×63.54×100 / 1000	Log x/m	Log Ce
4	0.1	0.0895	0.068	-1.7576	-0.04817
6	0.1	0.084	0.10168	-1.7709	-1.0757
8	0.1	0.078	0.1398	-1.7575	-1.1079
10	0.1	0.0735	0.1684	-1.77737	-1.1337
12	0.1	0.072	0.17794	-1.828	-1.14266
14	0.1	0.067	0.2097	-1.8245	-1.1739
16	0.1	0.065	0.2224	-1.8569	-1.1870
18	0.1	0.0625	0.2383	-1.8781	-1.2041

Chart 5



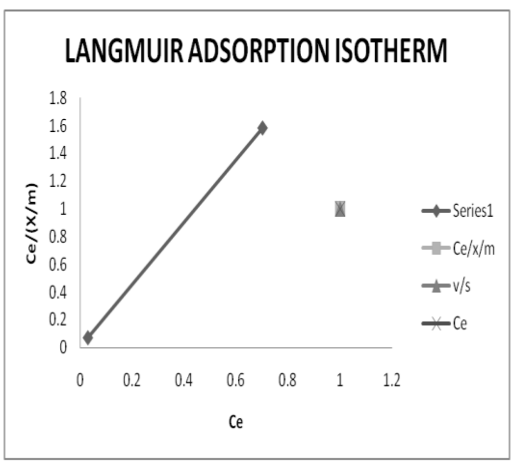
LANGMUIR ISOTHERM

Ce/(x/m)=1/bvm+c/vm

Table 6

Amt of TKP (g)	Initial concentration (Co)	Equlibrium concentration (Ce)	$X=(c_0-Ce)\times63.5\ 46\times100/1000$	X/m	Ce/x/m
4	0.1	0.0895	0.0667	0.0164	5.359
6	0.1	0.084	0.1017	0.01695	4.956
8	0.1	0.078	0.1398	0.017475	4.462
10	0.1	0.0735	0.1684	0.01684	4.364
12	0.1	0.072	0.17794	0.01271	5.6648
14	0.1	0.067	0.2097	0.01310	5.114
16	0.1	0.065	0.2224	0.0124	5.2419
18	0.1	0.625	0.2313	0.01191	5.252

Chart 6



SUGGESTIONS

Removal of heavy metal from industrial waste water is of primary importance because they not only cause contamination of water bodies but are also toxic to many life forms. Since most of heavy metals are non-degradable and toxic. So their concentration must be reduced to acceptable levels before discharging into environment, otherwise these can pose threat to public health .The metals of most immediate concern are zn,cr,Ni,Hg,Cu,Cd,Pb. Most of these enters to the environment as a result of human activities such as mining, purification of ores, steel production, coal burning, galvanization from waste water of pharmaceuticals, paints, pigments ,insecticides, cosmetics and industries. Adsorption generally used for the removal of toxic metals. Other methods such as ion exchange, chemical precipitation, ultra-filtration seen to be economically not feasible. Most commonly used low cost adsorbents are untreated plant's waste such as teak leaf powder, rubber leaf powder, papaya wood, news paper pulp, fly ash, banana and orange peels, carrot residue, tea waste etc. Hence it is possible to use for the removal of toxic Cu (II) from agricultural runoffs and from the industrial waste water.

SUMMARY AND CONCLUSION

The present study shows that the TKP was an effective bio adsorbent for the adsorption of Cu(II) ions from the aqueous solution. The effect of parameters like pH ,initial metal ion concentration and adsorbent concentration of equilibrium was studied.

The uptake of copper ions by TKP was increased with increase in adsorbent concentration and initial metal ion concentration. The uptake was also maximum at pH range 4.5-6. Above and below this range adsorption decreases.The proposed method is simple rapid and selective. It is suitable for separation of Cu,Cr,Hg etc. The present study shows that TKP can be used as an adsorbent for the removal of Cu(II)from waste water.

Our study reveals that the adsorption occurs in acidic medium. It follows Langmuir and Frenudlich isotherm

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