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Adsorptive removal of cadmium (II) ion from aqueous solution using plant biomass

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ABSTRACT

The adsorption of cadmium from aqueous solution on to Syzygium cumini.L has been studied using a batch adsorber. The parameters that affects the Cd(II) sorption, such as contact time, initial concentrations, solution pH, adsorbent dosage and adsorbent particle size, have been investigated and optimum conditions determined. Equilibrium isotherm studies were used to evaluate the maximum sorption capacity of syzygium cumini.L. The fitness of the biosorption data for Langmuir, Freundlich and Redlich-Peterson models was investigated. It was found that biosorption of Cd(II) on to the biomass of the syzygium cumini.L was better suitable to Langmuir than other two models. Using the Langmuir model equation, the monolayer biosorption capacity of syzygium cumini.L was evaluated and found to be 36.363mg/g.

KEYWORDS

Cadmium (II);
Syzygium cumini L.;
Biosorption;
Isotherms;
Equilibrium studies.

INTRODUCTION

The increase in industrial activities has intensified environmental pollution and the deterioration of some ecosystems, with the accumulation of pollutants such as heavy metals, synthetic compounds, etc. The pollution by heavy metals is of great concern due to potential health hazard caused by these compounds to the environment[1].

The heavy metal object of this study, cadmium is often released into the environment through industrial activities at concentrations of physiological and ecological concern. Cadmium is registered as List 1 in the Dangerous Substances Directive (2006/11/EC) of the European Union, while zinc and chromium are registered as List 2. The quality standards for cadmium are 1μg/L for estuaries and marine waters and 0.5μgL-1 for freshwater. Cadmium may be found in wastewater discharges from the electroplating industry, the manufacture of nickel–cadmium batteries, fertilizers, pesticides, pigments and dyes and textile operations[2,3]. The kidneys are the critical target organ after ingestion (renal dysfunction, hypertension and anaemia)[4].

Therefore, an adequate treatment of the polluted wastewater is required. Traditional treatment techniques include chemical precipitation, membrane filtration, electrolysis, ion exchange, carbon adsorption and co-precipitation/adsorption. Nevertheless, the application of such processes is sometimes restricted because of technical or economic constraints[5,6]. The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to biosorption, based on the metal binding capacities of various biological materials[7].

The adsorbent used in this study is plum leaves (*Syzygium cumini L*) powder, in which the adsorption takes place on surface of insoluble cell walls of the plum leaves. The insoluble cell walls of plum leaves are largely made up of cellulose and hemi celluloses, lignin, condensed tannins and structural proteins. In other words, one-third of the total dry matter in plum leaves should have good potential as metal scavengers from solutions and waste waters since the above constituents contain functional groups.

MATERIALS AND METHODS

Preparation of *Syzygium cumini L.* for adsorption

The green colored java plum leaves (*Syzygium cumini L.*) used in the present study were collected from the college of engineering, Andhra University, Visakhapatnam. The collected leaves were washed with deionised water several times to remove dirt particles. The washing process was continued till the wash water contains no dirt. The washed leaves were then completely dried in sunlight for 20 days. The resulting product was directly used as biosorbents. The dried leaves were then cut into small pieces and powdered using domestic mixie. In the present study the powdered materials in the range of 75-283μm. particle size were then directly used as biosorbent without any pretreatment.

Metal solution

Stock solutions of Cadmium concentration 1000 mg/L was prepared by dissolving 7.14 g of $Cd SO_4$ $8H_2O$ in 1000 ml of distilled water. The solution was prepared using standard flasks. The range of concentration of the prepared metal solutions varied between 20 and 100 mg/L. The solutions were prepared by diluting the Cadmium stock solution, which were obtained by dissolving in deionized water.

Chemicals

Metal ion solutions were prepared by diluting stock metal solutions, which were obtained by dissolving weighed quantity of $CdSO_4$ $8H_2O$ of analytical reagent grade obtained from Merck in double distilled water.

Biosorption experiments

Biosorption experiments were performed in a rotary shaker at 180 rpm using 250 ml Erlenmeyer flasks containing 30 ml of different cadmium concentrations. After one hour of contact (according to the preliminary sorption dynamics tests), with 0.1 g *Syzygium Cumini* L. leaves biomass, equilibrium was reached and the reaction mixture was centrifuged for 5 min. The metal content in the supernatant was determined using Atomic Absorption Spectrophotometer (GBC Avanta Ver 1.32, Australia) after filtering the adsorbent with watman filter paper. The amount of metal adsorbed by *Syzygium Cumini* L. leaves was calculated from the differences between metal quantity added to the biomass and metal content of the supernatant using the following equation:

$$Q = (C_o - C_f) \times \frac{V}{M} \tag{1}$$

where Q is the metal uptake (mg/g); C_o and C_f are the initial and equilibrium metal concentrations in the solution (mg/L), respectively; V is the solution volume (L); and M is the mass of biosorbent (g). The pH of the solution was adjusted by using 0.1 N HCl and 0.1 N NaOH.

RESULTS AND DISCUSSION

The adsorption of Cadmium (II) ions on the *Syzygium cumini L* was investigated as a function of the contact time, initial metal ion concentration, pH, adsorbent dosage and adsorbent particle size. The performance of *Syzygium cumini L* for Cadmium (II) removal using the experimental data for Langmuir, Freundlich and Redlich-Peterson adsorption isotherm was tested.

Effect of contact time

Time course profiles for the biosorption of Cadmium from a solution of 20 mg/L are shown in figure 1. The data obtained from the adsorption of Cadmium ions on the *Syzygium cumini L.* showed that a contact time of 20 min for Cadmium was required to achieve an optimum adsorption and there was no significant change in concentration of the metal ion with further increase in contact time. Therefore, the uptake and unabsorbed Cadmium concentrations at the end of 20

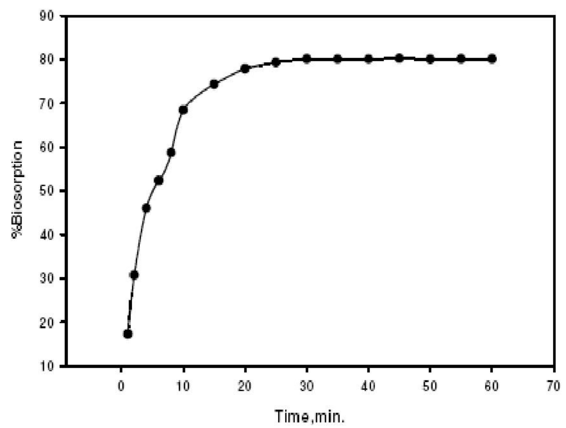

Figure 1 : Effect of contact time on biosorption of cadmium by *syzygium cumini L.* for 20 mg/L and 0.1g/30mL of biosorbent concentrations

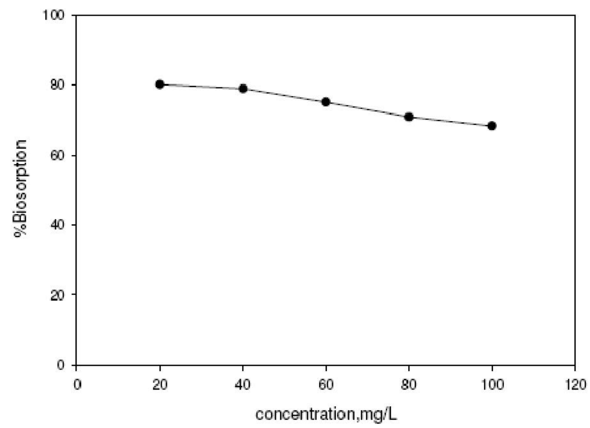

Figure 2 : Effect of metal ion concentration on the adsorption of cadmium by *syzygium Cumini L.* at 0.1g/30ml of adsorbent concentration

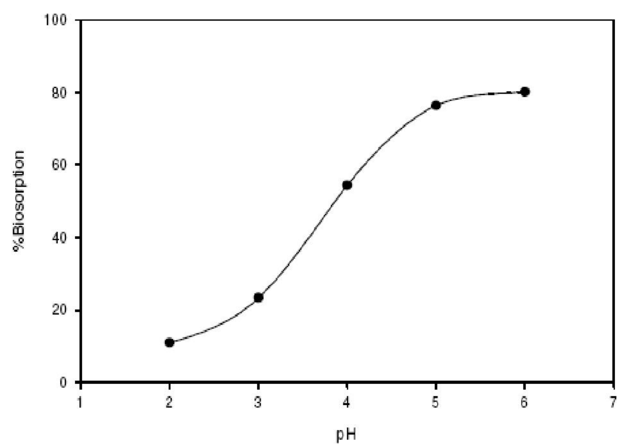

Figure 3 : Effect of pH on biosorption of cadmium adsorption by *syzygium Cumini L.* for 20 mg/L of metal and 0.1 g/30ml of biosorbent concentration

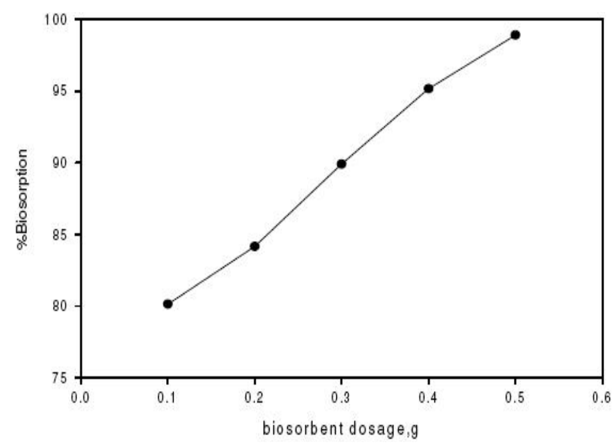

Figure 4 : Effect of biosorbent dosage on biosorption of copper and cadmium for 20mg /L of metal ion concentration

min are given as the equilibrium values, q_{eq} (mg/g) and C_{eq} (mg/L) as 36.363 and 4.809, respectively.

Effect of initial metal ion concentration

Experiments were undertaken to study the effect of the initial metal ion concentration on the Cadmium removal kinetics from the solution. The results obtained are shown in figure 2, the obtained curves show that the metal uptake increases and percentage adsorption of Cadmium (II) decreases with increase in initial metal ion concentration. The increase of metal uptake is a result of the increase in the driving forces i.e. concentration gradient, with an increase in the initial Cadmium ion concentrations (from 20 to 100 mg/L). However, the percentage biosorption of Cadmium ions on *Syzygium cumini L.* was decreased from 85.14to 70.12 and 80.15 to 68.26%.

Influence of pH

It is well known that the pH of the medium affects the solubility of metal ions and the concentration of the counter ions, on the functional groups of the biomass cell walls. Thus pH is an important parameter on biosorption of metal ions from aqueous solutions *Syzygium cumini L.* presents a high content of ionizable groups (carboxyl groups) on the cell wall polysaccharides, which makes it very liable to the influence of the pH. As shown in figure 3, the uptake of free ionic Cadmium depends on pH. The biosorption of metallic ion was observed to increase with increase in pH up to a value of 6. At pH values lower than 4.0 Cadmium removal was inhibited, possibly as a result of the competition between hydrogen and metal ions on the sorption sites, with an apparent preponderance of hydro-

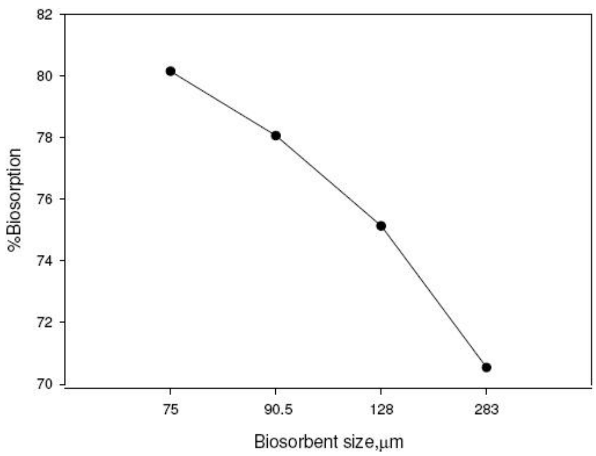

Figure 5 : Effect of biosorbent particle size on biosorption of copper and cadmium for 20 mg/L of metal and 0.1 g/30 ml of biosorbent concentration

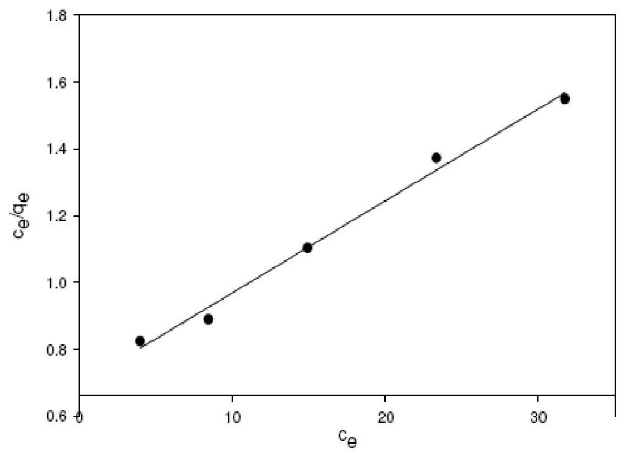

Figure 6 : Langmuir biosorption isotherm for cadmium at 0.1g/30ml of biosorbent concentration

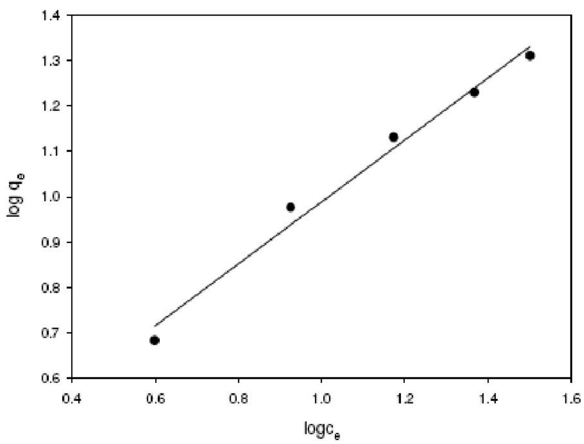

Figure 7 : Freundlich biosorption isotherm for cadmium at 0.1g/30ml of biosorbent concentration

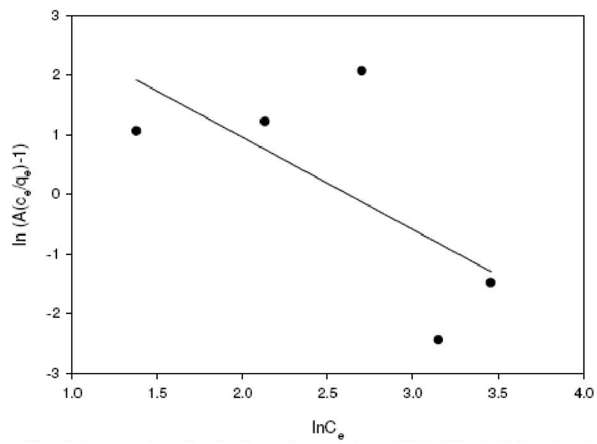

Figure 8 : Redlich-Peterson adsorption isotherm for cadmium at 0.1g/30 ml of biosorbent concentration

gen ions, which restricts the approach of metal cations as in consequence of the repulsive force. As the pH increased the ligands such as carboxylate groups in *Syzygium cumini L*. would be exposed, increasing the negative charge density on the biomass surface, increasing the attraction of metallic ions with positive charge and allowing the biosorption onto the cell surface.

Effect of adsorbent dosage

The influence of adsorbent dosage in removal of Cadmium (II) is shown in figure 4.The increase in adsorbent dosage from 0.1 to 0.5g resulted in an increase from 85.14to 98.03% in adsorption of Cadmium (II).This is because of the availability of more binding sites for complexation of Cadmium (II) ions.

Effect of adsorbent particle size

Fixing the initial concentration of solution at 20 mg/L, pH 6, the fixed volume of 30 ml solution is allowed for 20 min for Cadmium a adsorption with 0.1 g each of the varied size of particles of adsorbent ranging from 75 to 283 μm, the plot (Figure 5) drawn for the variation of the percentage biosorption against particle size, shows that with increase in particle size the adsorption decreases. This is due to less surface area available with increased particle size, thus reducing the adsorption.

Biosorption isotherm models

Many sorption isotherm models are usually used to fit the biosorption data in order to obtain a linear regression data to predict the maximum sorption capacity of the biosorbent. Langmuir and Freundlich models are the most widely used models in the case of the biosorption of metal ions with biosorbents. Redlich Peterson model also applied to describe equilibrium

TABLE 1 : Langmuir, Freundlich and Redlich-peterson isotherm constants and correlation coefficients

Langmuir model	Freundlich model	Redlich-peterson
q_{max}(mg/g)=36.363	K_f =2.0128	A(L/g)=0.792
b(L/mg)= 0.03957	M(g/L)=0.6846	B(L/mg)=57.11
R^2=0.991030315	R^2=0.985537502	R^2 =0.437078303

TABLE 2 : Comparison of the adsorption capacity of present work for Cadmium metal with those reported in the literature

Adsorbent	pH	Adsorption capacity(mg/g)	Reference
Modified bark	4.5	1.02	8
Turkish coals	4.0	0.8992	9
Granular biomass	5.5	60	10
Olive stone waste	5.5	0.0077	11
Fly ash	2-9	5	12
Marine green macro alga	6.0	3.95	13
Grape stalk waste	5.5	27.877	14
Papaya wood	5.0	0.48	15
Activated sludge	4.5	12.365	16
Syzygium cumini.L	6	36.3636	Present study

sorption isotherms. Langmuir model suggests monolayer sorption on a homogeneous surface without interaction between sorbed molecules. In addition, the model assumes uniform energies of sorption on to the surface and no transmigration of the sorbate.

The linearized Langmuir, Freundlich, Redlich adsorption isotherms obtained at room temperature are shown in figure 6, 7 and 8 and adsorption coefficients computed these are given in TABLE 1. All curves had good linearity (correlation coefficient)indicating strong binding of Cadmium(II) ions to the surface of *syzygium cumini L* particles. It is found that the adsorption of Cd(II) on the *Syzygium Cumini L.* was correlated well with the Langmuir equation as compared to Freundlich and Redlich-Peterson equations under the concentration range studied.

CONCLUSIONS

The present study shows that the Syzygium Cumini L. was an effective biosorbent for the biosorption of Cadmium ions from aqueous solution. The biosorption capacity of *Syzygium Cumini L*. was superior due to the higher content of hydroxyl and amine groups. The effect of process parameters like pH, metal ion concentration, biosorbent concentration and biosorbent size on process equilibrium was studied. The uptake of Cadmium ions by *Syzygium Cumini L*. was increased by increasing the metal ion concentration and the adsorbent concentration and decreased by increasing biosorbent size. The uptake was also increased by increasing pH up to 6. The adsorption isotherms could be well fitted by the Langmuir equation.

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