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Biosorption of Crystal Violet from Water on Leaf Biomass of *Calotropis procera*

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Abstract: The biosorption of a triphenylmethane dye, crystal violet from water on leaf biomass of *Calotropis procera*, a member of the family Asclepiadaceae, was studied. The effect of contact time, initial dye concentration and adsorbent dose were investigated. The biomass showed good removal efficiency for crystal violet from water. The adsorbent removed 80.48% of crystal violet from aqueous solution at a dye concentration of 20 mg L^{-1} (about 50 μM) in 60 min. The adsorption data fitted well into Langmuir adsorption isotherm showing monolayer coverage of the adsorbent surface. The Langmuir parameters, q_o and K_L were calculated to be 4.14 mg g^{-1} and 0.1139 L mg^{-1}, respectively. The kinetic data showed that the biosorption of crystal violet on the biomass obeys Lagergren first order rate expression. The rate of biosorption was rapid in the initial 5 min and then decreased gradually and attained equilibrium in 60 min. The rate constant came out to be 0.0322 min^{-1}.

Key words: Biosorption, crystal violet, *Calotropis procera*, Langmuir, kinetic, adsorbent

INTRODUCTION

Out of the many pollutants present in wastewaters, dyes affect the environment badly. Dyes are synthetic aromatic water soluble and dispersible organic compounds, which cause coloration of natural water bodies when released into the environment. They affect the aquatic fauna and flora by reducing light transmission through water surface and in some cases may be toxic to the aquatic biota due to the presence of aromatics, metals, chlorides etc. Dyes usually have complex aromatic molecular structures, which make them more stable and more difficult to biodegrade (Aksu, 2005).

Major classes of synthetic dyes include azo, anthraquinone and triphenyl-methane dyes. Dyes are difficult to degrade biologically, so that removal of dyes from aquatic environment has received considerable attention. About 10-15% of all dyes are directly lost to wastewater in the dyeing process (Vaidya and Datye, 1982). Thus the wastewater must be treated before releasing into the natural environment. The members of triphenylmethane family are animal carcinogens (Parshetti *et al*., 2006). The triphenylmethane dye, crystal violet, has been extensively used in human and veterinary medicine as a biological stain and in various commercial textile processes as a dye (Bumpus and Brock, 1988). Crystal violet has been classified as a recalcitrant molecule, thereby indicating that it is poorly metabolized by microbes and consequently is long lived in a variety of environments (Chen *et al*., 2007). An additional worrying factor is that some triphenylmethane dyes including crystal violet are potent clastogens, possibly responsible for promoting tumor growth in some species of fish (Cho *et al*., 2003).

Many alternative processes aimed at removing crystal violet from wastewater have been investigated including chemical oxidation and reduction, physical precipitation and flocculation, photolysis, adsorption, electrochemical treatment, advanced oxidation, reverse osmosis and

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biodegradation (Azmi *et al*., 1998). Of these, adsorption is known to be a promising technique, which has great importance due to the ease of operation and comparable low cost of application in the decolorization process. Various adsorbents have been tested and used for the removal of dyes from polluted water such as activated carbon, silica gel, natural clay, peat, wood chips, rice husk ash, living or dead microbial biomass etc. (Safarik *et al*., 2002).

In the present research, the biosorption of crystal violet from aqueous solution on leaf biomass of *Calotropis procera* has been investigated. The phytochemistry of this plant has revealed that its leaves and stalks contain calotropin, calotropagenin and phenolics. The aqueous extract of the leaves contains D-glucose, D-arabinose, D-glucosamine and α-rhamnose. Its latex contains uscharine, calotoxin, calactin, amyrin esters, uscharidin, voruscharine, uzarigenin, syriogenin, proceroside and choline. The seeds contain coroglaucigenin, frugoside and corotoxigenin. The root bark contains benzoyllineolone and benzoylisolineolane while the flowers contain calotropenyl acetate and procesterol.

MATERIALS AND METHODS

This study was conducted at the Department of Biotechnology, University of Malakand, Chakdara, Pakistan, in December 2007.

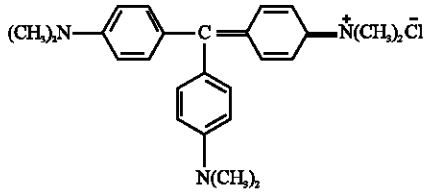
Preparation of Biosorbent

The leaves of *Calotropis procera* (giant milkweed or Sodom apple), an evergreen perennial shrub of the family Asclepiadaceae, were collected from its plants in Tazagram, a village near the University campus. The leaf biomass of the plant was chosen as biosorbent material because of its easy availability in greater amounts. The leaves were washed with distilled water and sun dried for seven days. The dried leaves were crushed and sieved to a final particle size of 120-160 μm. The powdered biomass obtained in this manner was kept in an oven at 105°C for 80 min in order to evaporate moisture.

Dye Solution

A stock dye solution (100 mg L^{-1}) was prepared by dissolving 100 mg of the pure dye in one liter of distilled water. Subsequent dye solutions were prepared by dilution of the stock dye solution. The property wise data of the dye is shown below.

CI number = 42555
CI name = Basic violet 3
λ_{max} = 593 (Gurr, 1971), 588 (Aldrich)
Empirical formula = $C_{25}H_{30}N_3Cl$
Structure,



Biosorption Experiments

Effect of Contact Time

One Hundred milliliter dye solution (30 mg L^{-1}) was shaken at 120 rpm at 20°C with 1 g of the adsorbent in 250 mL caped Erlenmeyer flasks for 80 min. The adsorption progress was monitored by

measuring the absorbance of the solution at various time intervals, 5, 10, 15, 20, 25, 30, 40, 50, 60 and 80 min. Each time a sample was taken out of the being treated solution, it was filtered using a disposable syringe filter (0.45 μm) and the absorbance of the filtrate was measured at the λ_{max} of the dye (588 nm) using a UV-Visible Spectrophotometer (UV-1700 Shimadzu). The extent of adsorption or removal of the dye was calculated from the decrease in absorbance of the solution by using the following equation:

$$\text{Removal (\%)} = \frac{A_o - A_t}{A_o} \times 100\,\%$$

Where:
A_o = Initial absorbance of the solution
A_t = Absorbance of the solution at time (t)

Effect of Initial Dye Concentration

For investigating the effect of initial dye concentration on adsorption, different initial dye concentrations (10, 20, 30, 40 and 50 mg L^{-1}) were used. The experiments were carried out as described earlier but the treatment was done for 60 min, the equilibrium time.

Effect of Adsorbent Dose

Hundred milliliter of dye solution (30 mg L^{-1}) was treated with different amounts of the adsorbent (0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 2.5 and 3.0 g) for 60 min and the above mentioned procedure was used.

All the experiments were carried out in duplicate and mean values were taken.

RESULTS AND DISCUSSION

Effect of Contact Time

The adsorption data for the removal of crystal violet from aqueous solution at a dye concentration of 30 mg L^{-1} (about 75 μM) is shown in Fig. 1. The equilibrium time for the adsorption of crystal violet on the adsorbent was 60 min (1 h). In the initial 5 min, the rate of adsorption was very rapid after which adsorption took place gradually. Thus 57.76% of the dye was removed in the first 5 min. The higher adsorption rate at the initial period (first 5 min) may be due to a large number of vacant sites on the adsorbent surface available at the initial stage (Uddin *et al*., 2007). As time passes, the adsorption rate is decreased due to the accumulation of the dye molecules in the vacant sites.

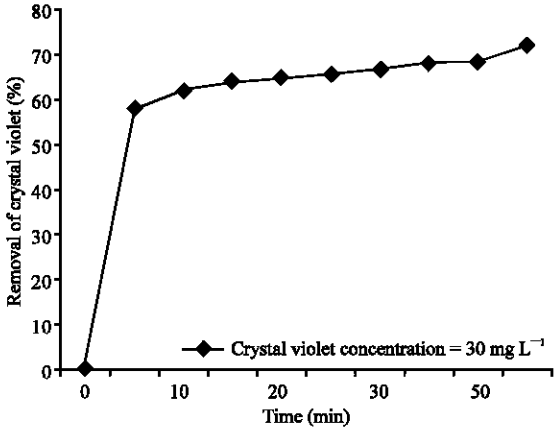


Fig. 1: Effect of contact time on the adsorption of crystal violet onto *Calotropis procera* leaf biomass

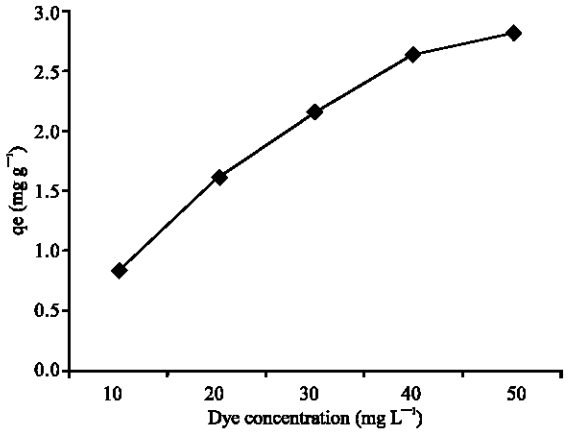


Fig. 2: Effect of initial dye concentration on the adsorption of crystal violet onto leaf biomass of *Calotropis procera*

Effect of Initial Dye Concentration

The adsorption of crystal violet, q_e (mg g^{-1}), was calculated by using Eq. 1 (Mahvi *et al*., 2007).

$$q_e = \frac{(C_o - C_e)\,V}{m} \quad (1)$$

Where:

q_e = Adsorption density (mg of adsorbate adsorbed per g of adsorbent)
C_o = Initial concentration of adsorbate (mg L^{-1})
C_e = Equilibrium concentration of adsorbate (mg L^{-1})
V = Volume of solution used (L)
m = Mass of adsorbent used (g)

From the data, it is seen that the removal of crystal violet, q_e (mg g^{-1}), increases with increasing initial dye concentration. The effect of initial dye concentration on adsorption of crystal violet onto leaf biomass of *Calotropis procera* is shown in Fig. 2.

Effect of Adsorbent Dose

The percentage removal of crystal violet increased with increase of adsorbent dose up to 1 g and then decreased. Figure 3 shows the effect of adsorbent dose on the adsorption of crystal violet onto leaf biomass of *Calotropis procera*. The increase in percentage removal with increase in adsorbent dose up to 1 g can be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase in adsorbent dose. The decrease in percentage removal at adsorbent doses of more than 1 g may be due to aggregation of the adsorbent particles thereby reducing the adsorbent surface area and hence number of adsorption sites.

Adsorption Isotherm

The equilibrium data for the adsorption of crystal violet onto leaf biomass of *Calotropis procera* was analyzed by using the Langmuir adsorption isotherm, which is the most widely used isotherm equation for modeling of the adsorption data and is valid for monolayer adsorption onto a surface with a finite number of identical sites. The Langmuir adsorption isotherm equation is given by Eq. 2.

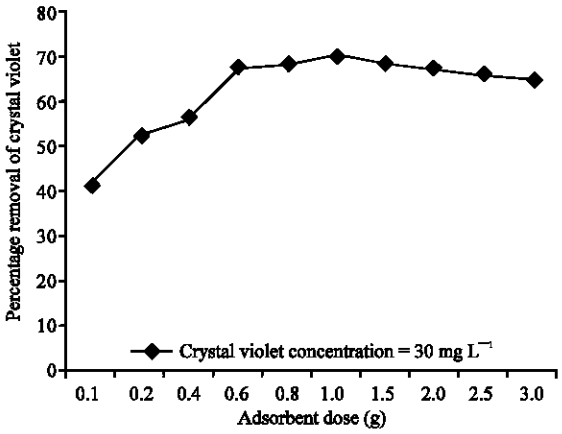


Fig. 3: Effect of adsorbent dose on the adsorption of crystal violet on leaf biomass of *Calotopis procera*

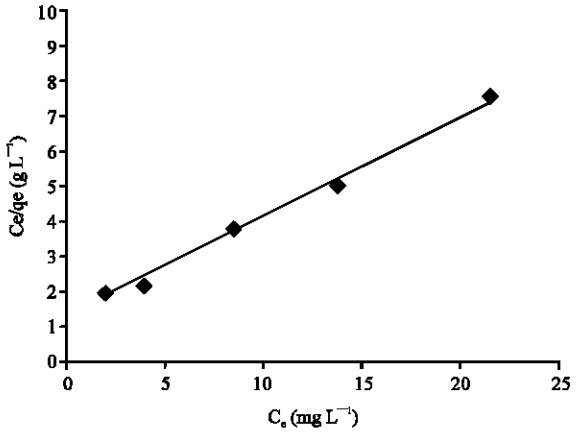


Fig. 4: Langmuir plot for crystal violet adsorption from aqueous solution on leaf biomass of *Calotopis procera* at 20°C

$$q_e = \frac{q_o K_L C_e}{1 + K_L C_e} \quad (2)$$

where, q_o and K_L are Langmuir parameters related to maximum adsorption capacity and free energy of adsorption, respectively. C_e is the equilibrium concentration in the aqueous solution and q_e is the equilibrium adsorption capacity of adsorbent. The linearized form of Langmuir equation can be written as:

$$\frac{C_e}{q_e} = \frac{1}{q_o K_L} + \frac{C_e}{q_o} \quad (3)$$

Straight line was obtained by plotting C_e/q_e vs. C_e as shown in Fig. 4. The applicability of the Langmuir isotherm indicates good monolayer coverage of the dye molecules on the surface of the leaf biomass of *Calotropis procera*, which consequently suggests the formation of monolayer coverage of adsorbate on the adsorbent surface in the concentration range studied. Langmuir constants, q_o and K_L

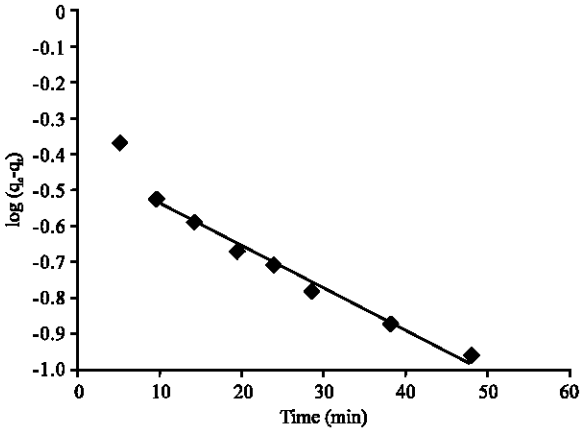


Fig. 5: Lagergren plot for crystal violet adsorption on leaf biomass of *Calotropis procera* at 20°C

were calculated from the slope and intercept of plot of C_e / q_e vs. C_e, respectively. The values of q_o and K_L are 4.14 mg g^{-1} and 0.1139 l mg^{-1}, respectively. Thus the maximum adsorption capacity of the leaf biomass of *Calotropis procera* was found to be 4.14 mg g^{-1}.

Adsorption Kinetics

In order to analyze the biosorption kinetics of crystal violet, the first order kinetic model was applied to the experimental data. The first order rate expression of Lagergren can be expressed as:

$$\log (q_e - q_t) = - \frac{k\,t}{2.303} + \log q_e \qquad (3)$$

where, q_e and q_t are the amounts of adsorbate adsorbed (mg g^{-1}) at equilibrium and at time t, respectively and k is the overall rate constant. Straight line was obtained by plotting log ($q_e - q_t$) vs. t as shown in Fig. 5. This indicates that crystal violet adsorption onto leaf biomass of *Calotropis procera* follows first order kinetics. The value of rate constant, k, was calculated from the slope of the plot of log ($q_e - q_t$) vs. t. The value of k was found to be 0.0322 min^{-1}.

Adsorption Mechanism, Nature of Adsorbent Sites and Type of Interaction Between Sites and Crystal Violet

The FT-IR studies of the biomass of *Calotropis procera* have confirmed the presence of aromatic groups, hydroxyl groups and carboxylic groups (Pandey *et al*., 2007). The biosorption of crystal violet on the leaf biomass of the plant may likely be due to electrostatic attraction between these groups and the cationic dye molecules (CV^+). At pH above 4, the carboxyl groups are deprotonated and as such are negatively charged. These negatively charged carboxylate ligands ($-COO^-$) can attract the positively charged crystal violet molecules and binding can occur. Thus the CV^+ binding to the biomass may be an ion-exchange mechanism, which may involve electrostatic interaction between the negatively charged groups in the cell walls and the dye cationic molecules.

CONCLUSION

The performance of the leaf biomass of *Calotropis procera* as biosorbent for textile dyes can be evaluated by comparing its dye uptake capacity with other biosorbents. Removal of crystal violet from aqueous solution at different concentrations, pH and temperatures by neem saw dust has been carried

out. The percentage of dye adsorbed was found to be 91.56 for the dye at a dye concentration of 6 mg L^{-1} at a temperature of 30±1°C and pH 7.2 (Khattri and Singh, 2000). Eren and Afsin (2006) investigated the adsorption of crystal violet from aqueous solution onto raw and pre-treated bentonite surfaces. According to their results, the amounts of crystal violet (CV^+) adsorbed at equilibrium at 298 K were 0.27, 0.37, 0.49 and 0.54 mmol g^{-1} bentonite for the raw, Ni-, Zn- and Co-saturated bentonite samples, respectively. The biological decolorization of a structurally related dye, malachite green using microalgae *Cosmarium* sp. was investigated by Daneshvar *et al*. (2007). Their results show that the algae (4.5×10^6 cells mL^{-1}) removed 80% of the dye at a dye concentration of 10 ppm at pH 9 and 25°C. Recently Ncibi *et al*. (2007) have studied the adsorptive removal of another dye, reactive red 228 using *Posidonia oceanica* fibrous biomass. According to them, the q_o (mg g^{-1}) at pH 5 and 30°C using the Langmuir model is 5.74. From the present study, it can be concluded that the leaf biomass of *Calotropis procera* is a potentially good adsorbent for the removal of crystal violet (a cationic dye) from aqueous solution. The cation binding capacity of the adsorbent biomass can be enhanced by its treatment with alkalis like sodium hydroxide. Most plant tissues have cellulose, hemicellulose and lignin as their major constituents. These constituents contain methyl esters, which do not bind metal ions (cations) significantly. The methyl esters can be converted to carboxylate ligands by treatment of a biomass with alkalis like sodium hydroxide. The resulting carboxylate ligands are believed to be responsible for binding metal ions (cations) (Rehman *et al*., 2006).

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