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Removal of Congo Red from Aqueous Synthetic Solutions Using Silica Gel Immobilized Chlorophyta Hydrodictyon Africanum

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ABSTRACT

A silica gel-chlorophyta hydrodictyon africanum biosorbent with improved mechanical properties was prepared and used in the removal of Congo Red (CR) from synthetic aqueous solutions. Batch sorption studies of the acidic dye showed that a maximum of 50.11 mg g^{-1} of the dye could be adsorbed under optimum conditions. Results show that maximum CR adsorption lie within the pH range 4-6. Above pH 6, the adsorption capacity dropped drastically to about 10.00 mg g^{-1} at pH 8. Kinetic data was simulated on three models and the pseudo-second order model gave a better fit with R^2 greater than 0.98. Equilibrium studies show that the adsorption of CR is best described by the Langmuir isotherm.

Key words: Immobilization, adsorption, Langmuir, Freundlich, biosorbent

INTRODUCTION

Since the discovery of the first synthetic dye, Mauveine in the mid-19th century, the number of dyes in the market now exceeds 100,000 with most being consumed in the textile industry. The textile industry now uses several hundred thousand tonnes of dyes annually worldwide (Ghaly *et al*., 2014). Production of large quantities of various textile dyes has, as a result, attracted the attention of environmentalists as the dying process is accompanied by large volumes of industrial dye effluent (Ghaly *et al*., 2014). Studies have shown that disposal of large quantities of dye effluent poses a serious danger to human health and aquatic life (Kant, 2012; Ratna and Padhi, 2012; Mathur *et al*., 2005). Currently established methods of dye effluent treatment include coagulation-flocculation-precipitation, sorption, electrochemical wastewater treatment and membrane filtration, advanced oxidation processes (Ong *et al*., 2011; Jain *et al*., 2004; Bidhendi *et al*., 2007). While these methods are routinely used in wastewater treatment, they have shown some limitations especially from an environmental view point.

Bio-sorption techniques for water treatment are continually being developed with the view of coming up with economic and environmentally friendly methods. Broadly, these techniques include use of bio-waste, activated carbon prepared from different bio-waste, microorganisms such as bacteria (Vijayakumar and Manoharan, 2012; Vijayaraghavan and Yun, 2008), fungi (Lacina *et al*., 2003), micro and macro alga (Abd-El-Kareem and Taha, 2012; Rubin *et al*., 2005).

In this article, we report a potential application of silica gel immobilized chlorophyta hydrodictyon africanum biosorbent for the removal of the acidic dye, Congo Red (Fig. 1). Chlorophyta hydrodictyon africanum is an algal species that grows widely in the Zimbabwean

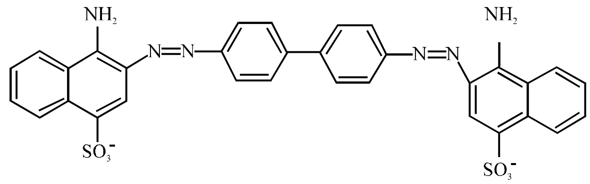

Fig. 1: Chemical structure of Congo Red

Table 1: Selected examples for removal of Congo Red using different adsorbents

Algae	Maximum adsorption (mg g^{-1})	References
Marine alga *Porhyra yezoensis ueda*	71.46 at 25°C	Wang and Chen (2009)
Chlorophyta hydrodictyon africanum	50.11 at 25°C	Present study
Peanut shell	15.09	Abbas *et al*. (2012)
Anilinepropyl silica xerogel	22.20	Pavan *et al*. (2008)
Banana peels	11.2	Annadurai *et al*. (2002)
Orange peel	7.9	Annadurai *et al*. (2002)
Coir pith activated carbon	6.7	Namasivayam and Kavitha (2002)

summer weather. Removal of Congo Red from aqueous solutions using different types of adsorbents has also been reported by other researchers. Selected examples are shown in Table 1.

MATERIALS AND METHODS

Equipment and chemical reagents: Concentrations of dye solutions were determined on a Genesy 10S UV/Vis spectrophotometer. An orbital shaker was used to shake adsorbents suspended in dye solutions. A Hanna instruments pH meter was used to monitor pH of solutions. Sodium silicate solution was of technical grade and was supplied locally by Zimbabwe Phosphate industries. Reagent grade sodium hydroxide, ammonia and hydrochloric acid were supplied by Skylabs (Pvt) Ltd. (South Africa). Congo Red used for sorption studies was purchased from Saarchem (Pvt) Ltd. (South Africa).

Adsorbent immobilization procedure: chlorophyta hydrodictyon africanum was immobilized into silica gel matrix using a previously reported procedure. Dried biomass (100-0.800 mg) was suspended in 25 mL of 6% sodium silicate (v/v). Eighteen percent HCl (v/v) was gradually added until the pH reached 7.3 by which gelling would have started. The gelling process was allowed to continue for 3 days. After normal workup procedure, the adsorbent was dried at 80°C. Particles of the adsorbent were sieved through a 150 µm-sieve. Biomass immobilization ranged from 100-400 mg alga per gram silica.

Characterization methods: The silica gel-immobilized chlorophyta hydrodictyon africanum was characterized in terms of the effect of contact time, pH, adsorbent dosage and initial dye concentration. Generally, the silica gel immobilized-biosorbent was suspended in 25, 50, 100 and 200 mg L^{-1} dye solutions at an optimum pH of 4 and a temperature of 25°C. The suspensions were shaken using an orbital shaker at 135 rpm. The initial dye concentration c_i and concentration c_e at specified time were measured using a UV/Vis spectrophotometer. The adsorption capacity of the immobilized alga was determined from the concentration difference of the solution, at the beginning and at equilibrium as following equation:

$$q_e = \frac{V(c_i - c_e)}{1000 \times m_{ads}} \quad (1)$$

where, c_i and c_e are initial and equilibrium dye concentrations, V the volume of the solution and m_{ads} mass of adsorbent.

RESULTS AND DISCUSSION

Effect of adsorbent immobilization: The degree of biomass immobilization was varied from 100-400 mg g^{-1}. The effect on dye adsorption capacity was investigated at optimum pH 4 and a temperature of 25°C. The results are illustrated in Fig. 2. From the Fig. 2 it can be observed that the absorption capacity increased with increase in the degree of immobilization up to 300 mg biomass per gram silica gel. This may be due to an increase in surface area up to an immobilization of 300 mg g^{-1}.

Effect of initial dye concentration: Initial dye concentration helps the system to overcome diffusive mass transfer resistance of all molecules between the sorbate and sorbent. The effect of initial dye concentration on adsorption capacity was investigated for the concentration range 25-200 mg L^{-1} at a constant temperature of 25°C and pH 4. Equilibrium sorption, as illustrated in Fig. 3 increased from about 13.61-50.13 mg g^{-1}.

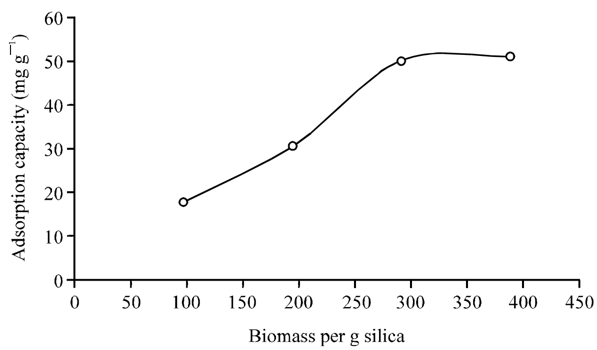

Fig. 2: Effect of the amount of biosorbent immobilization (t = 90 min, c_0 = 200 mg L^{-1} and pH 4)

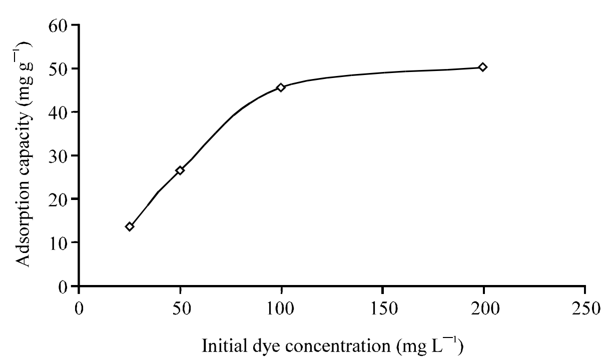

Fig. 3: Effect of initial dye concentration on adsorption capacity at optimum adsorption dosage and pH4

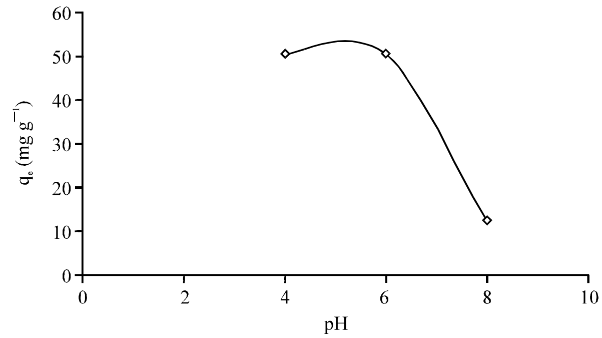

Fig. 4: Effect of pH on the adsorption capacity (c_0 = 200 mg L^{-1}, t = 90 min)

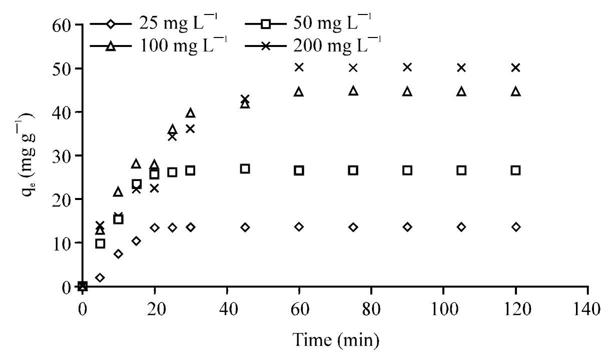

Fig. 5: Effect of contact time on adsorption capacity of silica gel immobilized chlorophyta hydrodictyon africanum for different initial dye concentrations

Effect of pH: The adsorption capacity of algal based adsorbents is pH dependent. This may be due to the role of functional groups present in the biomass at various pH values. These functional groups may include -NH_2, -OH and -COOH. The effect of pH was investigated in the pH range 4-8. From Fig. 4 it can be observed that maximum absorption capacity was between pH 4 and pH 6. Above 6, adsorption capacity dropped drastically to less than 10 mg g^{-1} at pH 8. At pH<4 Congo Red changed color and hence no experiments were carried out.

Effect of contact time: Contact time is an important parameter for the design of an adsorber or adsorption plant and shorter equilibration times are most desirable. The effect of contact time for dye concentrations 25, 50, 100 and 200 mg L^{-1} was studied for the duration period of 90 min at an optimum pH of 4. The result is illustrated in Fig. 5. As illustrated in the Fig. 5 the equilibration was achieved in 20 min for lower concentrations. The higher sorption rates in the first 20 min may be due to increased interactions between dye molecules and active sites on the biosorbent until saturation.

Kinetic models: Kinetic studies are carried out in order to design effective sorption systems. Psuedo-first and second order kinetic and the Weber-Morris models were used to fit kinetic data (Qiu *et al*., 2009; Tsibranska and Hristova, 2011).

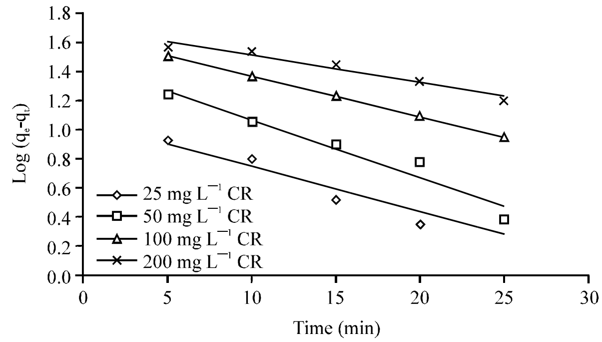

Fig. 6: Pseudo-first-order kinetic modelling of adsorption of CR on to silica gel immobilized Chlorophyta hydrodictyon africanum

Pseudo-first order kinetics is described by the following Eq. 2:

$$\frac{dq}{dt} = k_1 (q_e - q_t) \tag{2}$$

where, k_1 is the pseudo first order rate constant, q_e and q_t are the amounts of dye sorbed at equilibrium and after a certain time, respectively. Assuming t = 0, q_t= 0 and integrating Eq. 2 gave the Pseudo-first-order Kinetic Model of Lagergren in Eq. 3:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{3}$$

The pseudo-second-order rate equation is expressed as:

$$\frac{dq}{dt} = k_2 (q_e - q_t)^2 \tag{4}$$

where, k_2 is the second-order rate constant. Linearizing the integrated form (Eq. 4) gives:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

The parameters k_2 and q_e can be obtained from the intercept and the slope $\frac{t}{q_t}$ versust. The results for pseudo-first and second-order kinetic study are illustrated in Fig. 6 and 7. In Table 2 the kinetic data is shown and R^2 values suggest that the adsorption process is of the second order. Wang and Chen (2009) came to the same conclusion when the marine alga *Porphyra yezoensis* ueda as a biosorbent for the removal of Congo Red from aqueous solutions.

The Weber-Morris or intra-particle diffusion model describes the diffusion processes taking place between the solute molecules and adsorbent particles (Qiu *et al.*, 2009; Oladoja *et al.*, 2008). This model is given by:

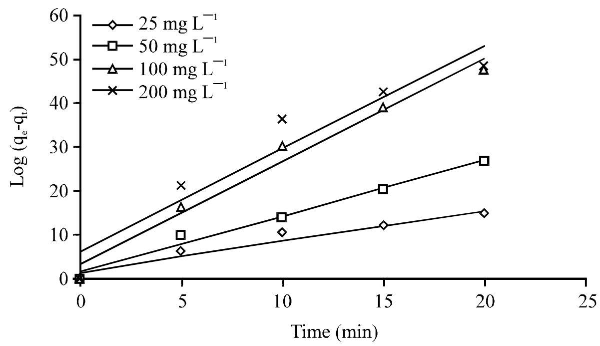

Fig. 7: Pseudo second order kinetic modelling of adsorption of CR on to silica gel immobilized Chlorophyta hydrodictyon africanum

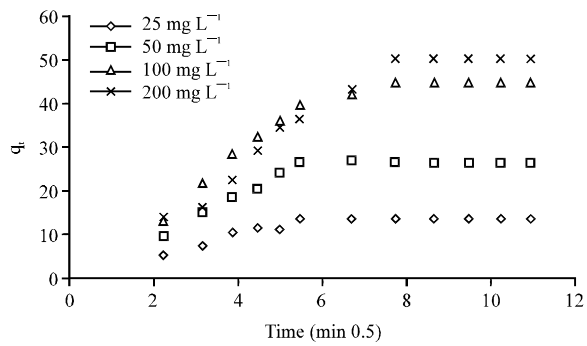

Fig. 8: Weber-Morris model for adsorption of Congo Red on silica gel-immobilized chlorophyta hydrodictyon africanum

Table 2: Pseudo-first and second order parameters for Congo Red adsorption

	First-order kinetic parameters			Second-order kinetic parameters		
Dye concentration (mg L^{-1})	k_1	q_e	R^2	k_2	q_e	R^2
25	0.0707	11.2610	0.8920	2.3518	14.5560	0.9965
50	0.0903	28.3727	0.9444	4.5331	28.2486	0.9960
100	0.0640	43.3910	0.9990	4.8077	49.7512	0.9965
200	0.0640	49.0343	0.9548	2.9214	60.9756	0.9879

$$q_t = k_{id}\sqrt{t} + c_{id} \tag{6}$$

where, k_{id} (mg g^{-1} $min^{-0.5}$) is the intra-particle diffusion rate constant and c_{id} is the intercept. The intercepts help to predict the effect of the boundary layer on the sorption process. The larger the intercept the larger the boundary layer effect. These parameters are determined from a plot of q_t against $\sqrt{t}$. The results for the Weber-Morris study are illustrated in Fig. 8, the k_{id} and R^2 values in Table 3. The k_{id2} values are very small compared to k_{id1}. This is an indication of a very slow diffusion process in the pores of biosorbent which may be attributed to the structure of Congo Red molecules.

Table 3: Weber-Morris parameters for the adsorption of Congo Red

Dye concentration	k_{id1}	R^2	k_{id2}	R^2
25	2.4647	0.9496	0.0003	0.1400
50	5.0093	0.9941	-0.0382	0.1567
100	8.1217	0.9947	0.8566	0.7141
200	7.6227	0.9593	2.3767	0.7121

Table 4: Isotherm parameters for the decoloration of Congo Red

Langmuir parameters			Freundlich parameters		
q_m (mg g^{-1})	k_L (L mg^{-1})	R^2	k_F ($mg^{1\text{-}1/n}L^{1/n}g^{-1}$)	n	R^2
75.1880	0.0953	0.9898	1.9476	1.5562	0.9211

Equilibrium studies: Equilibrium studies were carried out in order to establish the nature of adsorbate-adsorbent interaction. Experimental data was fitted on to the Langmuir and Freundlich isotherms. The Langmuir isotherm assumes monolayer homogeneous sorption sites whilst the Freundlich isother assumes heterogeneous sorption sites. The Langmuir equation can be expressed in its linearized form as:

$$\frac{1}{q} = \frac{1}{q_{m} c k_{ad}} + \frac{1}{q_m} \quad (7)$$

where, q_m is the monolayer adsorption capacity whilst c is the sorbate concentration in the solution at equilibrium (mg L^{-1}) and k_{ad} is the Langmuir adsorption constant. If a plot of 1/q against 1/c is linear, then the adsorption follows the Langmuir isotherm.

The Freundlich isotherm can be expressed as:

$$q = k_F c_e^{1/n} \quad (8)$$

where, c_e is the sorbate concentration at equilibrium (mg L^{-1}), k_F the Freundlich constant ($mg^{11-/n}L^{1/n}g^{-1}$) and n the sorption intensity. The integrated form of this equation is:

$$\log q_e = \log k_F + \frac{1}{n} \log c_e \quad (9)$$

The constants 1/n and k_F can be determined from the gradient and the intercept of the linear plot.

Parameters for the Langmuir and Freundlich isotherms for the adsorption of Congo Red are shown in Table 4. R^2 values show that adsorption process follows the Langmuir isotherm.

CONCLUSION

chlorophyta hydrodictyon africanum was immobilized in to silica gel matrix to improve its mechanical properties. The immobilized bio-sorbent was used in adsorption experiment of Congo Red. A maximum immobilization 400 mg biomass per gram silica. Results from adsorption experiments showed a maximum adsorption capacity of 50.11 mg g^{-1} at pH 4 and 25°C. Experimental data show that adsorption processes of second order rate. Experimental data fitted well with the Langmuir isotherm with R^2 = 0.9898.

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