ABSTRACT

Adsorption is a conventional process for removal of dyes from textile industry effluents. It is the simplest method as compared to other techniques and gains much importance in the waste water treatment especially those containing dyes. This work reports experimental studies on the adsorption characteristics of a low-cost natural adsorbent, Ricinus communis, i.e. castor leaf powder (CLP). The latter preparation involves collection of mature leaves from castor trees, washing in tap water, drying through the natural heat for 2 days and forced heat in a hot air oven at 105°C for two hours. CLP is then used to study the effect of various parameters on the initial dye concentration and the dye removal efficiency. The optimal process parameters of the dye–adsorbent system are determined. The optimal values of CLP dosage, the adsorption time and the stirrer speed are found to be 10 g/L, 2 h and 200 rpm, respectively. On the other hand, the dye removal efficiency decreases with increase of the initial dye concentration in the solution and the temperature, indicating that the adsorption process is exothermic and is efficient for the treatment of solutions of low adsorbate concentrations.

Keywords: adsorption, dye removal, wastewater treatment, Crystal Violet.

INTRODUCTION

Water is important for the survival of all form of life on the earth. But the industrialization and the mismanagement of the water resource have a huge adverse impact on the environment and living organisms. Water pollution is one of the problems which we face since long time but due to the rapid growth of the population and the urbanization, this problem becomes a severe one [1]. The major sources of polluted water refer to the textile, paint, and electroplating industries, the pulp mills, the dye manufacturing, the tanneries [2].

The water pollution caused by dye molecules is one of the greatest problems faced by the present society. The dye molecules have usually a high toxicity and poor degradability in the aquatic environment. Currently there is a growing awareness of these contaminants impact on the groundwater, the rivers, and the lakes. Therefore the removal of emerging contaminants is of great importance in the production of safe drinking water and the environmentally responsible release of wastewater [3, 8].

The treatment options which are typically considered for the removal of emerging contaminants from drinking water and wastewater refer to adsorption and application of advanced oxidation processes (AOPs), nanofiltration (NF), and reverse osmosis (RO) membranes. However, most of these methods involve complicated procedures requiring high investment and maintenance costs. They can lead to secondary pollution (generation of toxic sludge, etc.). On the other hand, the physicochemical treatments such as the coagulation/flocculation processes are generally found to be unable to remove endocrine disrupting compounds (EDCs), pharmaceuticals and personal care products (PPCPs). Although AOPs can be effective for the removal of emerging compounds, these processes can lead to the
formation of oxidation intermediates that are mostly unknown [4, 24]. In fact, the adsorption processes do not add undesirable by-products and have been found to be superior to other techniques for wastewater treatment in terms of design and operation simplicity, as well as insensitivity to toxic substances [11, 29]. Activated carbon is the oldest adsorbent known and is widely used for treatment of water due to its high adsorption capacity and surface area. Despite of its wide application area, its use on an industrial scale is quite limited because of the high cost input and the regeneration requirement. There are also other materials such as alumina, bauxite, silica gel, zeolites, agricultural wastes, used for the removal of different dye stuffs [5, 9, 28]. Clay and oil shale are used for the removal of cationic dyes from wastewater, while the adsorption parameters are found well fitted to a pseudo-second Langmuir model [22].

The use of agricultural solid wastes in removal of cationic and anionic dyes providing a simple comparison in terms of adsorption of substances of a different nature by a single adsorbent may possibly lead to a better understanding of the dye-classified adsorption process [14, 15, 31, 35] Azadirachta indica leaf powder is also explored for the removal of Congo red dye from aqueous solutions. It is observed that an amount of 0.6 g of the Neem leaf powder (NLP)/l can remove 52.0 % -99.0 % of the dye from an aqueous solution of a concentration of \(2.87\times10^{-2}\) mmol l\(^{-1}\) with agitation time increase from 60 min to 300 min [6]. Various low-cost non conventional adsorbents are used for dye removal. The numerous reports focus on: (i) the critical analysis of these materials; (ii) the description of their characteristics, advantages and limitations; and (iii) the discussions of the various mechanisms involved [8]. Guava (Psidium guajava) leaf powder (GLP) is used for the removal of methylene blue from an aqueous solution with a maximum dye uptake of 295 mg/g. This indicates that GLP can be used as an excellent low-cost adsorbent [25]. It is reported that orange peel adsorbent can be used for the removal of direct red 23 (DR23) and direct red 80 (DR80) dyes with a maximum adsorption of 97.7 % for DR23 and 93 % for DR80 in an aqueous solution of pH of 2 [7]. Various natural adsorbents for the removal of dyes from aqueous solutions are proposed. Formosa papaya seed powder is among them. It is found that it can remove crystal violet from an aqueous phase with a maximum adsorption capacity of 85.99 mg g\(^{-1}\) [26]. The Langmuir model is found adequate. Annona squamosa seed adsorbent is used for the removal of malachite green (MG) and methylene blue (MB) from aqueous solutions with a maximum adsorption capacity of 25.91 mg g\(^{-1}\) and 85.52 mg g\(^{-1}\), respectively [32]. Water hyacinth plant roots are used as a natural adsorbent for the removal of crystal violet dye from an aqueous solution. It is found that the corresponding Langmuir monolayer biosorption capacity amounts to 322.58 mg/g [34]. Sugar cane bagasse is also used in its natural and modified form as a natural adsorbent for malachite green dye removal [33]. The wide use of a commercial adsorbent such as activated carbon, clays, minerals, low cost adsorbents such as agricultural waste, industrial waste shows that adsorption is a green technology for removal of contaminants from waste water [21]. Coconut husk-based activated carbon is also studied for removal of crystal violet [23]. Clay/PNIPAm nanocomposite hydrogels of various clay contents are used for crystal violet removal. It is reported that the dye adsorption increases quickly within the initial 12 h reaching a maximum value of 4.71 mg/g at 25°C [27]. Wood apple shell (WAS) is used for the removal of, methylene blue (MB) and crystal violet (CV). It is found that WAS adsorption capacity for crystal violet (130 mg/g) is higher than that of methylene blue (95.2 mg/g) [12]. Treated ginger waste (TGW) is studied for crystal violet removal. It is found that the maximum capacity reaches 72.6 mg for 0.3 g TGW [16]. Palm kernel fiber can also remove crystal violet and methylene blue dyes from aqueous solutions. The experimental data obtained favor an adsorption process of a pseudo-second order [17]. Waste materials such as bottom ash and de-oiled soya (DOS) are studied for crystal violet removal through batch and column experiments [11]. The adsorption capacity of NaOH-modified rice husk is also explored to remove crystal violet. It is found that the adsorption proceeding is a spontaneous, exothermic and chemical in nature [18]. Low-cost NaOH treated saw dust is used for adsorption of brilliant green (BG) from an aqueous solution. The most suitable conditions refer to an initial pH of 2.9, contact time of 3 h and an
adsorbent dose of 4 g/l. A pseudo-second order kinetic model fits well the dye desorption [20]. BG adsorption on carbon rich bagasse fly ash is also studied. It is reported that the optimum conditions refer to an initial pH of 3.0, an adsorbent dose of 3 g/l and equilibrium time of 5 h. A pseudo-second-order kinetics is also found [10].

Homemade activated carbons prepared from Brazilian pine-fruit shell (Araucaria angustifolia) are used for the removal of brilliant green dyes from aqueous solutions [13]. Acorn based adsorbent is also used. It is found that 90% removal efficiency is obtained within 30 min at an adsorbent dose of 2 g/100 mL for initial dye concentration of 25 mg/L [19]. Deoiled soya, an agriculture waste material, and bottom ash, power plants waste, are used for the removal and recovery of the hazardous water-soluble dye brilliant green by a batch operation. Efforts are also made to recover the dye from exhausted columns by eluting sulfuric acid of pH of 3 [11].

A castor plant material is used in biodiesel production, silkworm breeding and heavy metals adsorption. A very limited literature is available for the treatment of different dyes by using castor leaf powder. The latter is used for the removal of heavy metals and mercury from wastewater [30]. There is no report on castor leaf powder use for textile dyes removal. This adsorbent is selected because of its abundant availability at no cost. The present study investigates the removal of crystal violet and brilliant green from an aqueous solution using castor leaf powder (CLP) as an adsorbent. Various operational parameters such as the solution pH, the temperature, the stirring speed, the contact time, the dosage of CLP, the initial dye concentration are studied in a batch mode. The adsorption data obtained are described by the Langmuir and Freundlich isotherm models, while the biosorption kinetics is followed using a pseudo-first-order, a pseudo-second-order and an intraparticle diffusion models. This study provides useful information on the scale up of the process of using CLP as a low cost adsorbent for various dyes removal.

EXPERIMENTAL
Adsorbent Preparation

Castor leaves were collected in a nearby area. They were thoroughly washed with tap water and subsequently with distilled water to remove all dirt and earthy materials. Then they were boiled in water for 3 h at 100°C to remove color or pigment components of the leaves. The leaves were dried with paper and then left for 2 days in sun. They were additionally dried in a hot air oven for 5 h at 105°C. The dried leaves were crushed and the powder obtained was sieved to a particle size of about 53 µm (BSS/Tyler No. 150). Then it was stored in a plastic bottle.

Adsorbate

Crystal violet (CV) and brilliant green (BG) dyes used in the study were purchased from Loba Chemicals, Mumbai, India. They were of an analytical grade (80% purity) and used without further purification. Stock solutions (100 mg/l) were prepared. They were further diluted to the desired concentration. The dyes structure is shown in Figs. 1 and 2. The maximum absorbance ($\lambda_{\text{max}}$) of CV and BG were found at 588 nm and 625 nm, respectively.
Characterization of the adsorbent used

CLP was prepared from mature castor leaves using proper washing, drying and grinding. It was boiled after the grinding to remove the coloring component. Then it was sieved to reach a particle size of 53 µm.

Adsorption experiments

The adsorption rate and the corresponding equilibrium reached were studied. The experiments were carried out in 1000 ml glass beaker with 500 ml working volume of CV and BG solutions of a varying concentration. The solution pH was checked and adjusted by adding a few drops of standard solutions of (0.1N) HCl/NaOH. A fixed amount of CLP was added to the solution. The latter was then agitated at a desired speed on a constant temperature shaker using a mechanical stirrer. In each experiment one of the parameters studied was varied, while the rest of the parameters stayed constant. This was done to analyze the effect of pH, the temperature, the stirring speed, the initial adsorbate concentration, the adsorbent concentration and the contact time. The samples were collected for analyzing the residual dye concentration in the solution by using UV-Vis spectrophotometer at a wavelength of 588 nm and 625 nm for CV and BG, correspondingly. The uptake of the dye adsorbed per unit of CLP at time t, \( q_t \) (mg g\(^{-1} \)), was calculated using Eq. (1), while the dye removal \( R \) (%) of dye was estimated on the ground of Eq. (2):

\[
q_t = \frac{C_0 - C_f}{m} \cdot V
\]

\[
R = \frac{C_0 - C_f}{C_0} \cdot 100
\]

where \( C_0 \) was the initial dye concentration (mg L\(^{-1} \)), \( C_f \) was the current concentration of the dye, \( V \) was the volume of the solution (L), while \( m \) was the mass of CLP (g).

RESULTS AND DISCUSSION

Characterization of the adsorbent prepared

The morphological structure of CLP material obtained by using Jeol, JSM 5800 scanning electron micrograph is shown in Fig. 3 (a, b, c). The bulk composition is estimated by an indirect method with the

Table 1. EDXS analysis of CLP adsorbent.

<table>
<thead>
<tr>
<th>Element</th>
<th>C K</th>
<th>Mg K</th>
<th>Si K</th>
<th>S K</th>
<th>K K</th>
<th>Ca K</th>
<th>Cu K</th>
<th>Zn K</th>
<th>Zr L</th>
<th>Pt M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight (%)</td>
<td>75.08</td>
<td>0.52</td>
<td>0.45</td>
<td>1.54</td>
<td>6.21</td>
<td>6.21</td>
<td>3.89</td>
<td>3.70</td>
<td>2.60</td>
<td>1.71</td>
</tr>
<tr>
<td>Atomic (%)</td>
<td>92.52</td>
<td>0.32</td>
<td>0.24</td>
<td>0.71</td>
<td>1.67</td>
<td>2.25</td>
<td>0.91</td>
<td>0.84</td>
<td>0.42</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Fig. 3. SEM images of CLP adsorbent at different magnifications (100 µm, 50 µm, 10 µm).
application of SEM/EDXS. The elemental composition of the samples is initially determined (SEM/EDXS) and then percentages of the oxides present is calculated. The results are shown in Table 1.

**Effect of the initial solution pH on the dye adsorption**

Solution pH strongly affects the dye removal efficiency. That is the reason to carry out the adsorption experiments at pH values varying between 2 and 12. The plot of CV and BG removal efficiency versus pH is shown in Fig. 4(a) and 4(b). It is evident that CV removal efficiency increases with pH value increase as the dye used is an acid one, while CLP surface is positively charged. But at pH higher than 8, there are less attachment sites available due to the decreased positive charge of CLP surface. The optimal value of pH is found within the 8 - 10 range. BG removal efficiency increases with pH value increase of the solution until a maximum value is reached at pH of 12. Thus pH of 8 and 12 are chosen for the subsequent experiments with CV and BG, correspondingly.

**Contact time effect**

The effect of the adsorption time on the dye removal efficiency is followed for both dyes within the interval of 0 min - 480 min. The corresponding dependences are presented in Fig. 5(a) and 5(b). It is clearly seen that the removal efficiency increases with the adsorption time increase.

**Adsorbent concentration effect**

The effect of the adsorbate concentration on CV and GB removal efficiency is followed using adsorbent concentration values of 1 g/l, 2 g/l, 5 g/l, 10 g/l, 15 g/l and 30 g/l. The corresponding dependences are shown in Fig. 6(a) and 6(b).

It is seen that the removal efficiency increases with CLP concentration increase up to 10.00 g/L for CV and 15.00 g/L for BG. No significant improvement in the removal efficiency values is observed beyond this value. Thus, the optimal CLP concentration chosen is 30 g/L. Initially, the adsorption rapid increase with the increase in the adsorbent presence can be attributed to the
Fig. 5(a). CV percentage removal vs. adsorption time.

Fig. 5(b). BG percentage removal vs. adsorption time.

Fig. 6(a). CV percentage removal vs. adsorbent bulk concentration.

Fig. 6(b). BG percentage removal vs. adsorbent bulk concentration.
availability of greater surface area and hence increased adsorption sites. Then the adsorption is slowed down due to the adsorbate shortage in the solution.

**Dyes concentration effect**

The effect of the initial dye concentration on the removal efficiency is investigated in the course of experiments carried out with a dye concentration varying between 2 mg/L and 300 mg/L. The dependences obtained for CV and BG are shown in Fig. 7(a) and 7(b), respectively.

The figures presented show that the removal efficiency decreases with the initial dye concentration increase, i.e. the adsorption process is more effective at low dye concentrations.

**Ultrasound effect**

The effect of the ultrasound on the dye removal efficiency is studied in the course of experiments of varying ultrasound duration between 0 min and 120 min. It is illustrated in Figs. 8(a) and 8(b).

It is seen that the removal efficiency in respect to both dyes increases with increase of the ultrasound duration within 80 min. Then it decreases together with adsorption capacity decrease.

**Temperature effect on the dye adsorption**

The adsorption experiments are conducted at 20°C, 40°C and 60°C to analyze the effect of temperature on the dye removal efficiency. The corresponding plots are shown in Figs. 9(a) and 9(b), respectively. It is clearly seen that the temperature increase leads to increase of CV removal efficiency and decrease of that of BG. This indicates that the latter process is exothermic.

**Stirring speed effect**

Stirring is an important parameter affecting adsorption. The effect of the stirrer speed on the dye removal efficiency is studied in the course of experiments carried out at a stirrer speed varying between 0 rpm and 300
Fig. 8(a). CV percentage removal vs. ultrasound times variation.

Fig. 8(b). BG percentage removal vs. ultrasound times variation.

Fig. 9(a). CV percentage removal vs. temperature variation.

Fig. 9(b). BG percentage removal vs. temperature variation.
rpm. The corresponding plots are illustrated in Figs. 10(a) and 10(b), respectively.

It is seen that CV maximal removal occurs at 200 rpm, while for BG it is reached at 300 rpm.

**Adsorption equilibrium and kinetics**

The adsorption equilibrium of CV and BG is studied at four different temperatures. The Langmuir and Freundlich models are used to describe the data obtained.
adsorption capacity at different stirrer speeds. The values
of the pseudo-first-order model constants $k_1$ and $q_e$ are
calculated from the slope and the intercept of the plots of
$\ln (1 – q_t/q_e)$ vs. $t$ while the pseudo-second-order model
constants, $k_2$ and $q_e$ are calculated from the slope and
the intercept of the plots of $t/q_t$ vs. $t$. The slope of the
straight line referring to $–\ln (1–q_t/q_e)$ vs. $t$ is expected to
go through the origin of the coordinate system. It pro-
vides the estimation of the value of the pseudo first-order
rate constant $k_1$. The experimental data is not found fit
to the pseudo first-order model in case of CV removal.
The value of $k_1$ amounts to 0.0128 min $^{-1}$. The value of
regression coefficient is very low.

The value of $k_1$ found for BG amounts to 0.01 min $^{-1}$,
while the regression coefficient value is 0.859.

The calculated value of $q_e$ is in good agreement with
that obtained experimentally. This indicates that the
adsorption of CV and BG on CLP follows the pseudo-
second-order kinetic model. The values of $q_e$ and $k_2$ can
be obtained from the slope and intercept of the linear
dependence of $t/q_t$ vs. $t$, which are found equal to 1.0737
and 6.5092 for CV are 1.0737 and 6.5092. The regression
coefficient value is close to 1.0 (0.9991). Thus, $q_e$
(0.9313 mg/g) is exactly matching the experimental
value of 0.9313 mg/g, while $k_2$ is estimated equal to
0.1771 g mg $^{-1}$ min$^{-1}$.

The slope and the intercept of $t/q_t$ vs. $t$ (Fig. 12c)
plot referring to BG have values of 1.0998 and 15.046,
correspondingly. The regression coefficient value is also
close to 1.0 (0.9988). The value of $q_e$ (0.9092 mg/g) is
found exactly matching the experimental one, while the
value of $k_2$ is 0.0803 g mg $^{-1}$ min$^{-1}$.

The pseudo-second-order rate constant, $k_2$ increases
with stirring speed increase suggesting an external mass-
transfer resistance at low stirring speeds. Intraparticle
pore diffusion of the adsorbate ions is probable in a
batch adsorption system. It can even limit the process
rate. That is why this possibility is explored by using

Fig. 12(a). Pseudo first-order kinetic model of CV ad-
sorption on CLP surface.

Fig. 12(b). Pseudo first-order kinetic model of BG ad-
sorption on CLP surface.

Fig. 12(c). Pseudo second-order kinetic model of CV ad-
sorption on CLP surface.

Fig. 12(d). Pseudo second-order kinetic model of BG ad-
sorption on CLP surface.
the intra-particle diffusion model. In this case a plot of \( q_t \) versus \( t^{0.5} \) yields a straight line passing through the origin. However, the data can refer to multi linear plots, which in turn shows that the process is governed by two or more steps. The plots of CV and BG adsorption on CLP at different stirrer speeds based on intra-particle diffusion model are shown in Figs. 13(a) and 13(b). The first linear region is attributed to the external surface adsorption when the adsorbate diffuses through the solution to the external surface of the adsorbent. The negative values of the intercepts (CI) of the first linear parts indicate that the external diffusion is fast and does not offer much resistance to the mass transfer. On the other hand, the increasingly positive values for the intercepts (CI) of the second linear parts indicate that the pore diffusion can exert some resistance to the overall rate and that back diffusion/desorption may become possible at high stirring speeds. The values of \( k_i \) and \( C_i \) can be directly determined as the slope and the intercept of the linear plot of \( q_t \) versus \( t^{0.5} \). The corresponding values obtained for CV refer to 0.0153 mg/g min\(^{-1}\) and 0.6669 mg/g. Those for BG are 0.0218 mg/g min\(^{-1}\) and 0.5075 mg/g, respectively.

**CONCLUSIONS**

CLP can be used as a cost-effective natural adsorbent for the removal of CV and BG from their aqueous solutions. The adsorption capacity of CLP in respect to CV increases with increase of the dye initial concentration, the solution pH, the contact time, the ultrasonication time, the system temperature and the stirring speed but decreases with increase of the adsorbent concentration. The adsorption capacity in respect to BG increases with increase of the dye initial concentration, the solution pH, the contact time, the ultrasonication time and the stirring speed but decreases with increase of the adsorbent concentration and the system temperature. Best adsorption results are obtained for CV at pH of 8, while those for BG refer to pH of 10. The optimum adsorption time for both dyes is 2 h. The optimal stirrer speed is found equal to 200 rpm and 300 rpm for CV and BG removal, respectively. Optimum dosage of the adsorbent amounts to 10 g/l. The Langmuir isotherm fits well the equilibrium adsorption data indicating that the adsorption takes proceeds to a monolayer on the homogeneous adsorbent surface in absence of any interaction between the adsorbed species.

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