Adsorption of Congo Red from Aqueous Solution using Typha australis Leaves as a Low Cost Adsorbent

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Abstract

The aim of present work was to study the application of natural monocotyledonous flowering plants to remove an anionic dye (Congo red, chosen as a pollutant model) from wastewater. Batch adsorption experiments were carried out for the removal of Congo red from aqueous solutions using Typha australis leaf as a low cost adsorbent. The influence of contact time, solution pH, ionic strength, and initial adsorbate concentration was investigated. The experimental data fitted well with the Langmuir isotherm (\( R^2 = 0.95 \)), yielding a maximum adsorption capacity of 24.23 mg/g at 40 °C. The adsorption kinetic data were analyzed using the Pseudo First Order (PFO) and Pseudo Second Order (PSO) models. The results showed that the PSO model is the best for describing the adsorption of Congo red by Typha australis leaves for all initial Congo red concentrations. The thermodynamic parameters have been studied, and it proved that, adsorption of Congo red using Typha australis leaves is exothermic and spontaneous. This study convinced that the naturally Typha australis leaves proved to be an alternative, attractive, effective, economic and environmentally friendly adsorbent for Congo red removal from aqueous solutions.

Keywords: Congo red, Adsorption, Typha australis leaves, Kinetics, Isotherms

1 Introduction

Growing demand for commercial dyes in various industries has led to the mass production of dyes. More than 1.00x10^6 types of commercial dyes are available, with annual output exceeding 7.00x10^6 tons, most of them are directly discharged into the aqueous medium [1]. Due to their content of aromatic hydrocarbons, metals and chlorides, the dyes present in natural water, can reduce transparency, harm the growth of animals and plants and affect the solubility of oxygen and the self-cleaning process [2]. And because of their high solubility in water, dyes can be displaced in the river, affecting water quality [3]. Among the dye, Congo red [1-naphthalene sulfonic acid, 3, 30-(4, 40-biphenylenebis (azo)) bis (4-amino-) disodium salt], is a very harmful dye. Therefore, it is very much needed to remove these life threatening pollutants from wastewater before their final disposal to the environment [4; 5]. In order to reduce and eliminate this threat, several physico-chemical methods, such as photocatalysis [6], biodegradation [7], coagulation-flocculation [8], ozonation [9], membrane filtration [10] and adsorption [11] have been employed. Among all these methods, adsorption is the most popular treatment process for the removal of dye from an aqueous solution due to its simplicity in operation, high treatment efficiency without discharging any harmful by-products, easy recovery and the reusability of the adsorbent [12]. Although activated carbon is the most commonly used adsorbent, it has high cost and has difficulty in disposal [13]. Thus naturally occurring resources have drawn attention of many researchers. For this reason, researchers have concentrated on finding alternative natural adsorbents to commercial activated carbon. Natural adsorbents are preferred for their biodegradable, non-toxic nature, low commercial value and highly cost-effective nature. A number of non-conventional and low cost agro wastes sorbents have been tried for removing Congo red from aqueous solution via adsorption process [14-16]. The goal of this study is to investigate the possibility of using Typha australis, an abundant and available plant along the Senegal River, for the adsorptive removal of Congo red from aqueous solutions. In this regard, effects of different operating parameters such as adsorbent dosage, effect of contact time, initial dye concentration and ionic strength on the removal amount were studied. An efficient and

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comparative study of the adsorption process was investigated on the basis of kinetics, thermodynamics and isotherm results.

2 Material and methods

2.1 Chemicals

Congo red is a heterocyclic aromatic chemical compound with chemical formula: \(C_9H_7N_3NaO_3S_2\) and molecular weight of 696.7. Its chemical name is sodium salt of benzidine-bis-1-naphthylamine-4-sulfonic acid. Congo red used in this study was of analytical grade and used without further purification. All other chemicals used in this study were of analytical reagent grade. All the solutions are prepared using pure Congo red and distilled water. The stock solution is prepared by adding 1 g of the Congo red to 1 L of distilled water. Other concentrations are prepared by dilutions of the stock solution and used to develop the standard curves using the Spectrophotometer UV1800 Rayleigh.

2.2 Collection, preparation and characterization of Typha australis

Biomass of Typha australis growing along the Senegal River was collected from the city of Rosso, Wilaya of Trarza, from Mauritania. The collected materials were washed thoroughly with distilled water to remove dirt. The biomass was then air dried for 3 days followed by drying in an oven at 105 °C for 24 h. The dried biomass was ground, sieved to obtain particle sizes below 0.5 mm and stored in a dessicator before use. The physicochemical characteristics are reported [17; 18].

2.3 Batch adsorption studies

Congo red adsorption using Typha australis leaves as adsorbent conducted in batch experiments. Batch adsorption experiments were carried out by varying several experimental variables such as adsorbent dosage (0.1-1.8 g), contact time (0–90 min), initial concentration (5–30 mg L\(^{-1}\)) and ionic strength (0.005-0.1 mol L\(^{-1}\)) at pH 2 to determine the optimum uptake conditions for adsorption. The effect of temperature on the amount of Congo red removed was studied at temperature of 20, 30 and 40 °C. In all sets of experiments were stirred (150 rpm).

The adsorption isotherms were obtained by varying the initial Congo red concentrations from 2.5 to 100 mg L\(^{-1}\). At the end of each experiment, the stirred solution mixture was centrifuged and the residual concentration of Congo red was analyzed by Spectrophotometer UV1800 Rayleigh at 655 nm wavelength. The adsorption uptake at equilibrium time \(q_e\) (mg g\(^{-1}\)) and percentage of the Congo red removed (%) are expressed by following equations (1) and (2), respectively:

\[
q_e = \frac{(C_i - C_e)V}{m}
\]

\[
\text{Removal} (%) = \frac{C_i - C_e}{C_i} \times 100
\]

where \(q_e\) is the Congo red concentration in adsorbent (mg g\(^{-1}\)), \(C_i\) is the initial Congo red concentration (mg L\(^{-1}\)); \(C_e\) is the Congo red concentration at equilibrium (mg L\(^{-1}\)); \(V\) is the solution volume (L) and \(m\) is the mass of the Typha australis leaves as adsorbent used (g). All batch experiments were conducted in triplicate and the average values are reported.

3 Results and discussion

3.1 Effect of adsorbent mass

Biomass dosage is an important parameter in adsorption studies, as it gives the optimum dose at which maximum adsorption occurs. The effect of the amount of Typha australis leaves adsorbent on the efficiency of adsorption was also studied. Variation of doses in the range 0.1–1.8 g at a fixed Congo red concentration (10 mg L\(^{-1}\)) for Congo red removal by Typha australis leaves is shown in Figure 1.

![Figure 1: Effect of adsorbent dosage on the adsorption of Congo red by Typha australis leaves](image_url)

The results suggest that the increase in the dose of adsorbent results in an increase in adsorption, probably due to increase in the retention surface area. However, further increase after a certain dose not improve the adsorption; perhaps due to the interference between binding sites of the Typha australis leaves adsorbent at different doses. Similar phenomenon was reported for Methylene Blue adsorption using same Typha australis leaves as low cost adsorbent [17]. The optimal Typha australis adsorbent dose obtained is 0.2 g.

3.2. Effect of contact time and Congo red initial concentration

The effects of contact time and Congo red initial concentration on the adsorption uptake using Typha australis leaves at 20 °C are shown in Figure 2.

![Figure 2: Kinetics of Congo red adsorption by Typha australis leaves for various initial dye concentrations](image_url)

Figure 2 showed that the adsorption of Congo red increase with time till it reached a constant value beyond which no more
Congo red was further removed from the solution. The necessary time to reach equilibrium is variable according to the initial concentration of dye: about 90 min for $C_0 = 5$ mg L$^{-1}$, 60 min for $C_0=10$ mg L$^{-1}$, 50 min for 20 mg L$^{-1}$, 60 min for 30 mg L$^{-1}$ and 60 min for 50 mg L$^{-1}$. The initial faster rates of adsorption may also be attributed to the presence of large number of binding sites for adsorption and the slower adsorption rates at the end is due to the saturation of the binding sites and attainment of equilibrium. Similar results have been previously reported in the literature for dye removal [15]. From figure 2, it was also shown that the adsorption of Congo red increased with an increase in initial dye concentration and this confirmed strong chemical interactions between Congo red and Typha australis leaves adsorbent. This is due to increasing concentration gradient, which acts as increasing driving force to overcome all mass transfer resistances between the aqueous solution and solid phase. Similar observations have been reported in the literature for dye removal [15].

3.3. Effect of ionic strength

The ionic strength of the solution is an important parameter that controls both electrostatic and non-electrostatic interactions between dyes and membrane surfaces. The effect of inorganic salt (NaCl) on adsorption of Congo red on Typha australis is presented in figure 3. As seen in figure 3, the presence of inorganic salt has influenced the percentage of the Congo red removed. The Congo red adsorption decreases with the increasing NaCl concentration. These results may relate to the competition between Congo red anions and Cl$^-$ (from NaCl) for the active adsorption sites, in good agreement with previous reports [19; 20].

![Figure 3: The effect of ionic strength on Congo red removal (%)](image)

3.4 Study of adsorption kinetics and thermodynamic

To study the adsorption mechanism, which governs the adsorption procedure, and to estimate whether the adsorption mechanism can be considered as a physical or chemical mechanism, various adsorption models, such as PSO and PFO models were applied to investigate the adsorption data. The nonlinear kinetics PFO and PSO models may be expressed by (3) and (4), respectively:

$$q_t = q_e (1 - \exp^{-k_1 t})$$

(3)

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

(4)

where $q_t$ is the amount of Congo red adsorbed per unit mass of Typha australis leaves (mg g$^{-1}$) at time $t$, $k_1$ (L min$^{-1}$) is the PFO rate constant, $k_2$ (mg g$^{-2}$min$^{-1}$) is the PSO rate constant for adsorption, $q_e$ (mg g$^{-1}$) is the amount of Congo red adsorbed at equilibrium and $t$ is the contact time (min). Figures 4, 5, and 6 shows that adsorption kinetic data for the adsorption of Congo red onto Typha australis leaves. The adsorption kinetic parameters values and $R^2$ values were calculated using Solver Excel. The calculated values were listed in Table 1.

![Figure 4: PFO and PSO non linear for Typha australis adsorbent with initial Congo red concentration of 5 mg L$^{-1}$](image)

![Figure 5: PFO and PSO non linear for Typha australis adsorbent with initial Congo red concentration of 10 mg L$^{-1}$](image)

![Figure 6: PFO and PSO non linear for Typha australis adsorbent with initial Congo red concentration of 20 mg L$^{-1}$](image)
A high value of $R^2$ of PSO model was achieved for Congo red, which indicated that this adsorption model is more fitted with the adsorption data than the PFO model. These suggested that the PSO adsorption mechanism was predominant and that the overall rate of the Congo red adsorption process appeared to be controlled by chemical process involving valence forces through sharing or exchange of electrons between Congo red dye and *Typha australis* leaves. It was also observed that the PSO rate constant ($k_2$) decreased with increased initial concentration. Similar kinetics was also observed in adsorption methylene blue on papaya seeds [21], biosorption of malachite green onto poly(lactide/spent brewery grains films [22] and adsorption of Congo red dye on cattail root [23]. From the thermodynamic calculations $\Delta G^\circ$ values for *Typha australis* (-4.03 kJ mol$^{-1}$) being negative revealed that the mechanism of Congo red adsorption from the aqueous solution is feasible and shows spontaneity. The negative value of $\Delta H^\circ$ (-18.04 kJ mol$^{-1}$) indicated the exothermic process. Similar results for exothermic adsorption were observed on adsorption on pine bark [24]. The negative value of $\Delta S^\circ$ (-35.86 J mol$^{-1}$) suggested a decrease in randomness at the solid/liquid interface, and that no significant changes occurred in the internal structure of *Typha australis* during Congo red adsorption.

3.5 Adsorption isotherm

To evaluate the efficacy of the adsorption process, two adsorption models, namely, Langmuir and Freundlich models, were employed. A monolayer adsorption is defined by the Langmuir model upon the homogeneous surface of the adsorbent and represented as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$  \hspace{1cm} (5)

where $q_e$ is the amount of Congo red adsorbed per unit mass of *Typha australis* leaves adsorbent (mg g$^{-1}$), $k_L$ is the Langmuir constant related to the adsorption capacity (L g$^{-1}$), $C_e$ is the concentration of Congo red in the solution at equilibrium (mg L$^{-1}$), $q_m$ is the maximum uptake per unit mass of *Typha australis* leaves adsorbent (mg g$^{-1}$). A multilayer adsorption is described by the Freundlich model upon the heterogeneous surface of sorbent material and illustrated as:

$$q_e = K_F C_e^{1/n}$$  \hspace{1cm} (6)

where $K_F$ (mg g$^{-1}$) (L mg$^{-1}$)$^n$ and $1/n$ are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The results obtained from Langmuir and Freundlich equations are illustrated in Table 2. Langmuir model is a better model to explain the adsorption isotherm based on $R^2$ values. As shown in Figures 8, 9 and 10, the maximum adsorption capacity of *Typha australis* for Congo red at 20, 30 and 40 °C was 17.40, 21.85 and 24.23 mg g$^{-1}$, respectively. In addition, it was observed that the maximum adsorption capacity was found to increase with increase in temperature of the solution. This observation confirms that the dye uptake process is exothermic in nature.

### Table 1: Non-linear kinetic model parameters

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>5 mg L$^{-1}$</th>
<th>10 mg L$^{-1}$</th>
<th>20 mg L$^{-1}$</th>
<th>30 mg L$^{-1}$</th>
</tr>
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<tbody>
<tr>
<td>PFO</td>
<td>$q_{exp}$</td>
<td>0.273</td>
<td>0.843</td>
<td>1.798</td>
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<tr>
<td></td>
<td>$q_e$</td>
<td>0.253</td>
<td>0.814</td>
<td>1.797</td>
<td>2.653</td>
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<tr>
<td></td>
<td>$K_1$</td>
<td>0.393</td>
<td>0.81</td>
<td>1.02</td>
<td>1.04</td>
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<tr>
<td></td>
<td>$R^2$ (%)</td>
<td>91.50</td>
<td>97.53</td>
<td>98.77</td>
<td>98.45</td>
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<tr>
<td>PSO</td>
<td>$q_e$</td>
<td>0.267</td>
<td>0.836</td>
<td>1.768</td>
<td>2.699</td>
</tr>
<tr>
<td></td>
<td>$K_2$</td>
<td>2.21</td>
<td>2.02</td>
<td>1.53</td>
<td>1.04</td>
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<td></td>
<td>$R^2$ (%)</td>
<td>96.63</td>
<td>97.91</td>
<td>99.59</td>
<td>99.19</td>
</tr>
</tbody>
</table>

Figure 7: PFO and PSO non linear for *Typha australis* adsorbent with initial Congo red concentration of 30 mg L$^{-1}$

### Table 2: Langmuir and Freundlich isotherm models constants and $R^2$ for the adsorption of Congo red by *Typha australis* leaves

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>20 °C</th>
<th>30 °C</th>
<th>40 °C</th>
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<tr>
<td>Langmuir</td>
<td>$q_m$</td>
<td>17.40</td>
<td>21.85</td>
<td>24.23</td>
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<td></td>
<td>$K_L$</td>
<td>0.052</td>
<td>0.032</td>
<td>0.024</td>
</tr>
<tr>
<td></td>
<td>$R^2$ (%)</td>
<td>95.17</td>
<td>94.56</td>
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<tr>
<td></td>
<td>$1/n$</td>
<td>0.72</td>
<td>0.79</td>
<td>0.82</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_F$</td>
<td>1.061</td>
<td>0.81</td>
<td>0.68</td>
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<tr>
<td></td>
<td>$R^2$ (%)</td>
<td>93.58</td>
<td>93.40</td>
<td>94.91</td>
</tr>
</tbody>
</table>

Figure 8: Comparison between the experimental and predicted isotherms for the adsorption of Congo red by *Typha australis* leaves adsorbent at 20 °C.
4 Conclusions

The adsorption of Congo red dye onto *Typha australis* was found to be dependent on adsorbent dosage, contact time, initial dye concentration and ionic strength. Adsorption kinetics was well-described with the PSO model. Thermodynamic properties indicated that the adsorption process was spontaneous and exothermic in nature. The adsorption isotherm for *Typha australis* fitted better for Langmuir isotherm model compared to Freundlich isotherm model. Due to the *Typha australis* low cost, technical and economic feasibility, abundant availability, environmental benefits, high adsorption capacity and eco-friendly, it can be utilized as a promising adsorbent for dyes removal in the future for efficient large scale Congo red removal from industrial wastewater. For future studies, the usability of *Typha australis* for dyes removal from real wastewater will be tested and as comparison, a fixed bed column will be employed to investigate the effect of reactor design.

**Ethical issue**

Authors are aware of, and comply with, best practice in publication ethics specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

**Competing interests**

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

**Authors’ contribution**


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