

## UTILIZATION OF WATER HYACINTH FOR DYE EFFLUENT PURIFICATION

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Water hyacinth (*Eichhornia crassipes*) (WH) is an invasive plant floating freely on the water, which is widely spread in tropical and subtropical regions. The plant is characterized by high porosity and a high number of functional groups, such as hydroxyl (-OH), carboxyl (-COOH), and amino groups (-NH<sub>2</sub>). Activated carbon, which is widely accepted on an industrial level for the adsorption of dyes from wastewaters, is a highly expensive material. Thus, in this research, a bioadsorbent material was prepared based on WH biomass and investigated as an alternative tool for water quality remediation, in the case of dye pollutants (RR HE3B). The WH plants were collected from the nearby Lake Tana and used as an adsorbent material without chemical treatment. The batch adsorption test was performed by varying the pH of the solution, adsorbent dosage and initial dye concentration. The powdered WH and RR HE3B dye loaded WH were characterized using FTIR, revealing the emergence of new stretching vibration peaks in the range from 2800 to 3000 cm<sup>-1</sup> on the spectrum of Reactive Red HE3B (RR HE3B) dye loaded WH, confirming that -CH and -CH<sub>2</sub> were responsible for the adsorption. The analysis of the adsorption isotherm and of the suitability of different models for describing it has led to the following order: Freundlich > Langmuir > Temkin > Dubinin-Radushkevich, based on their correlation coefficient value. This implies that the WH adsorbent surface is heterogeneous and the adsorption of the dye onto it depends not only on the specific reaction sites, as the n-value of the Freundlich constant confirms that the physical adsorption process might be favored. Therefore, WH could be a potential alternative adsorbent to remove the RR HE3B dye from dye polluted wastewaters.

**Keywords:** water hyacinth (*Eichhornia crassipes*), Reactive Red HE3B dye, adsorption isotherm, bioadsorbent

### INTRODUCTION

Water hyacinth, with its local name Emboch, is an invasive weed harmfully spreading on Lake Tana, as well as various rivers in Ethiopia. Water hyacinth has become a growing concern in Africa, as its fast proliferation causes environmental, social and economic problems.<sup>1</sup> The largest lake in the world – Lake Victoria – has also become a victim of this invasive weed in Africa.<sup>2</sup> Water hyacinth is listed as one of the most productive plants on earth.<sup>2,3</sup>

Textile industries consume dyes extensively for enhancing the aesthetic appearance of textiles.<sup>4</sup> Most of them are synthetic and aromatic organic compounds, which are normally used for coloration of various textile materials. However, dyes are difficult to remove from the resulting effluent by a single treatment technique, as they have considerable structural diversity. They are recognized easily, even at levels of less as 1 ppm.<sup>5</sup>

The color of textile effluents intensifies environmental problems, mainly because of the non-biodegradable characteristics of dyes.<sup>4,6</sup>

While the textile industries are nowadays the backbone of economy for many developing countries, the dye polluted effluents represent a serious environmental concern. During textile processing, dyeing inefficiencies result in large amounts of dyestuff (varying from 2% loss when using basic dyes to 50% loss when certain reactive dyes are used)<sup>7</sup> being directly transferred to the wastewater, which would ultimately find a way into the environment.

The problem is even more serious when considering the huge amounts of water consumed by the textile industry. It has been reported that the general consumption of water is doubling every two decades, although, a reduction of this period is expected, if current trends in water use

persist.<sup>9</sup> In textile production, water consumption is estimated to be around 160 lbs. per 1 lb of textile product.<sup>10</sup> Of this, 72% of the water is estimated to be consumed for wet processing,<sup>11</sup> after which the wastewater is usually released to the water bodies.

The techniques practiced for the treatment of textile industry effluents include physicochemical, biochemical, combined and other advanced treatments.<sup>7</sup> The physicochemical approaches that have gained industrial acceptance for effluent treatments are equalization and or/homogenization, floatation, coagulation, flocculation, sedimentation, adsorption, and others.<sup>12</sup> From these physicochemical techniques, adsorption has been reported to be a simple and efficient approach.<sup>7,13</sup>

On an industrial level, activated carbon is often used for wastewater treatment by adsorption, but this makes the process expensive.<sup>7</sup> On the other hand, bioadsorbents have been reported to be cheap to produce, from abundantly available raw materials, non-toxic and highly efficient due to their high numbers of binding sites, high selectivity and adsorption capacity.<sup>14</sup>

It has been established that the fresh water hyacinth plant contains 95.5% moisture, 0.04% N, 1.0% ash, 0.06% P<sub>2</sub>O<sub>5</sub>, 0.20% K<sub>2</sub>O, 3.5% organic matter. On a zero-moisture basis, it constitutes 75.8% organic matter, 1.5% N, and 24.2% ash. The ash contains 28.7% K<sub>2</sub>O, 1.8% Na<sub>2</sub>O, 12.8% CaO, 21.0% Cl, and 7.0% P<sub>2</sub>O<sub>5</sub>. The crude protein (CP) consists of (per 100 g) 0.72 g methionine, 4.72 g phenylalanine, 4.32 g threonine, 5.34 g lysine, 4.32 g isoleucine, 0.27 g valine, and 7.2 g leucine (Fig. 1).<sup>8</sup> The plant has been investigated for the treatment of household and industrial wastewater, as well as for nutrients absorption from wastewater with some success.<sup>15,16</sup>

With these considerations, water hyacinth was studied in this paper as a bioadsorbent to remove Reactive Red HE3B dye from aqueous solution with expected double benefits: finding an alternative cheap material for treating textile effluents and exploiting an invasive weed, which threatens, by its proliferation, the biodiversity of local ecosystems. This approach could be the answer to the need to protect water bodies from the invasion of this weed plant, as well as to the sustainability in the production of biosorbents.

## EXPERIMENTAL

### Adsorbent

Water hyacinth was collected from Lake Tana, Bahir Dar, Ethiopia, and was used as an adsorbent material without chemical treatment. The plant was thoroughly washed with water to clean it from dust and other soluble materials, and allowed to dry at room temperature. The dried plant was crushed into fine powder and sieved through 200-300 mesh size. The overall experimental process is summarized in Figure 2.

### Adsorbate

Reactive Red HE3B dye was supplied by Merck (India). A stock solution of RR HE3B dye was then prepared (100 mg/L) by dissolving a required amount of dye powder in deionized water. The stock solution was diluted with deionized water to obtain 25, 50, 75 and 100 mg/L concentration. The chemical structure of RR HE3B dye is illustrated in Figure 3.

### Analysis

The residual concentration (A%) of RR HE3B dye in the treated solutions was determined from the standard curve obtained by measuring the absorbance of different known concentrations of RR HE3B dye solutions at  $\lambda_{max}$  543 nm, using a UV-vis spectrophotometer (Perkin Elmer Lambda 25, Singapore).

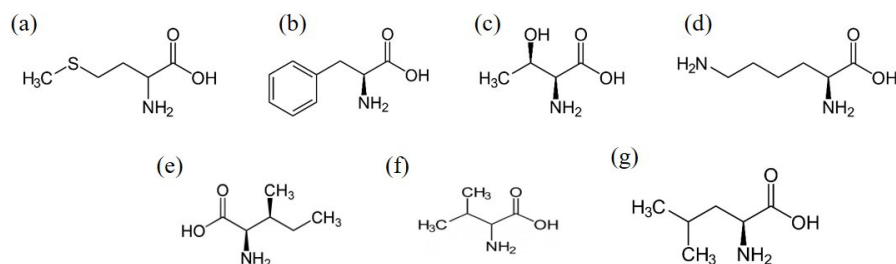


Figure 1: Chemical structure of methionine (a), phenylalanine (b), threonine (c), lysine (d), isoleucine (e), valine (f), and leucine (g)

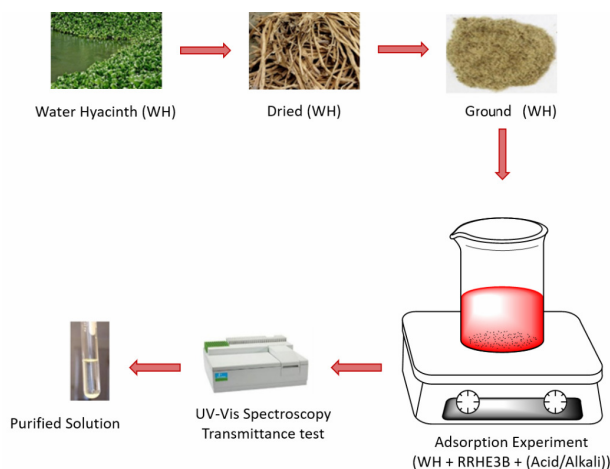


Figure 2: Summary of the experimental work where the water hyacinth samples is collected, dried, crushed and finally characterized

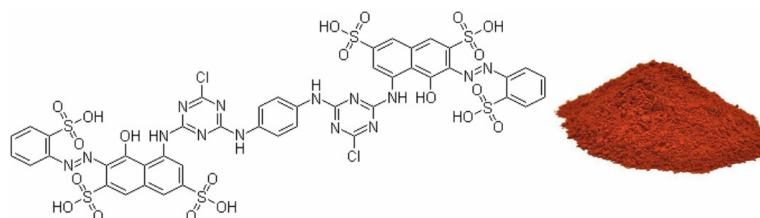


Figure 3: Structure of Reactive Red HE3B and a powdered sample

### Adsorption experiment

Adsorption experiments were conducted by varying pH, WH dose and initial concentration of RR HE3B dye. The experiments were carried out in 500 mL flasks and the total volume of the reaction mixture was kept at 250 mL. The solution pH was maintained at a desired value by adding 0.1 M NaOH or HCl. The solutions were stirred for the required time (120 min) at a constant stirring rate, using a magnetic stirrer at 30 °C. At the predetermined time, the flasks were withdrawn from the stirrer and kept for 12 h to settle. After this period, the residual dye concentration of the samples was analyzed by measuring the absorbance at the maximum wavelength ( $\lambda_{\text{max}}$  543 nm) of the dye. The residual dye concentration of the sample was calculated from the standard curve.

The equilibrium study was conducted by varying the initial concentration of RR HE3B from 25 to 100 mg/L. An amount of 3 g of WH with 250 mL of RR HE3B dye solution of various initial concentrations were stirred at 250 rpm for 120 min at 30 °C. All experiments were performed in duplicates. The amount of dye adsorbed onto WH,  $q_e$  (mg/g), was determined using Equation 1:

$$q_e = \frac{(C_i - C_e)V}{W} \quad (1)$$

where  $C_i$  and  $C_e$  are the initial and equilibrium concentrations (mg/L) of RR HE3B dye solution

respectively;  $V$  is the volume (L); and  $W$  is the mass (g) of the adsorbent.

## RESULTS AND DISCUSSION

### Characterization of WH adsorbent

The adsorption of RR HE3B dye onto WH depends mainly on the functional groups available on the surface of the adsorbent. The dye molecules get attached to the fiber by reacting with the available functional groups, as well as due to van der Waals and other forces. The FTIR spectra of WH and RR HE3B dye loaded WH are shown in Figure 4. The WH is characterized by O-H and N-H stretching in the wavenumber range of 3000-3600  $\text{cm}^{-1}$ , with a peak at 3288  $\text{cm}^{-1}$ . This peak shifted on the spectrum of the RR HE3B dye loaded WH to 3337  $\text{cm}^{-1}$ , exhibiting higher intensity. The stretching band between 2800-3000  $\text{cm}^{-1}$  is assigned to CH- and CH<sub>2</sub>- bands. The presence of new stretching vibration peaks in this range on the RR HE3B dye loaded WH confirms the adsorption of the dye on the WH, -CH- and CH<sub>2</sub>- being responsible for the adsorption. The stretching near the wavenumber 1700  $\text{cm}^{-1}$ , which varies in intensity between the WH and the RR HE3B dye loaded WH, is due to the C=O group.<sup>17</sup>

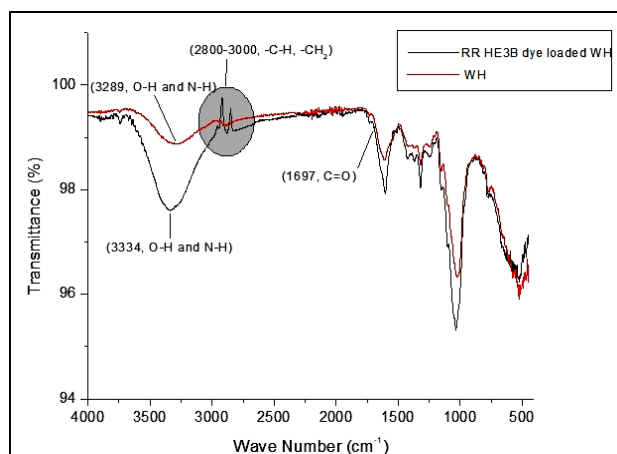


Figure 4: FTIR spectra of WH and RR HE3B dye loaded WH

### Effect of pH

The pH of the solution exerts a profound effect on the adsorptive uptake of RR HE3B dye molecules, presumably due to its influence on the surface properties of the WH and ionization/dissociation of the RR HE3B dye molecules. The variations in the removal of RR HE3B dye from solutions at various pH values are shown in Figure 5. From the figure, it is evident that the maximum removal of dye is observed at pH 4. At this pH value, there would be an increase in  $H^+$  ion concentration in the system and the surface of the WH acquires positive charge by absorbing  $H^+$  ions (Fig. 6). As the WH surface is positively charged at lower pH, a significantly strong electrostatic attraction appears between the positively charged WH surface and the anionic dye molecules, leading to maximum adsorption of the dye.

At pH 10, the dye molecules should acquire a negative surface charge, which would hypothetically lead to lower adsorption behavior of the dye onto the adsorbent;<sup>18</sup> while the experimental results obtained in this study indicated an increment in dye sorption. This can probably be explained by the fact that the WH is a lignocellulosic biomass, and was used in the adsorption experiments in the present work without any treatment. The adsorbent is expected to adsorb not only with the available functional groups, but also through the pores. Thus, as the contact area between the dye molecule and the WH adsorbent increased, the purification tendency also rose. At pH 7, both types of particles acquired a negative surface charge,

which led to lower adsorption. However, a different result was obtained for the adsorbent dosage of 12 g, which may be explained to the biosorption capacity of the WH adsorbent.

The hydrogen ion released in acidic media acts in neutralizing the surface charge of the water hyacinth cellulose, as shown in Figure 6. Also, water hyacinth naturally has a protein component, which is illustrated in Figure 1. These proteins will develop a positive charge in the media, through the presence of amine groups in their functional groups. The negatively charged RR HE3B dyes can easily approach the neutralized cellulosic surfaces and get adsorbed. Thus, the adsorption of RR HE3B dye in acidic media onto the water hyacinth biosorbent will be carried out both by charge neutralization and through the pores.

### Effect of adsorbent dosage

Figure 7 shows the plot of % RR HE3B dye removal against the adsorbent dose. It can be noted that the % RR HE3B removal varied with varying sorbent mass, increasing with a rising adsorbent dose. It is evident from the data that the maximum adsorption was obtained at the adsorbent dosage of 3 g at pH 4 and an initial dye concentration of 25 mg/L. The reduction of RR HE3B dye adsorbed onto the adsorbent,  $q_e$  (mg/g), with increasing WH dosage, might be explained by the variation in the concentration gradient between RR HE3B dye concentration in the solution and the RR HE3B dye on the surface of the WH. Therefore, with increasing the dosage of WH, the amount of dye adsorbed per unit weight of WH gets reduced, which results in a decrement of  $q_e$  (mg/g) with increasing WH dose.<sup>19</sup>

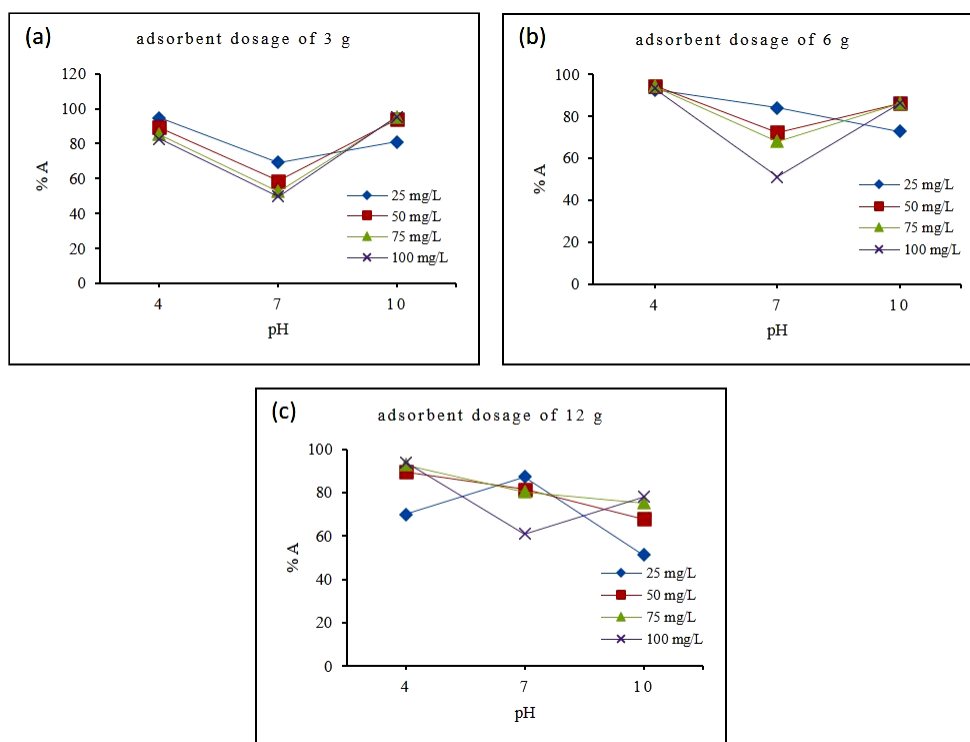


Figure 5: Effect pH on adsorption capacity of WH towards RR HE3B dye at adsorbent dosages of 3 g (a), 6 g (b) and 12 g (c)

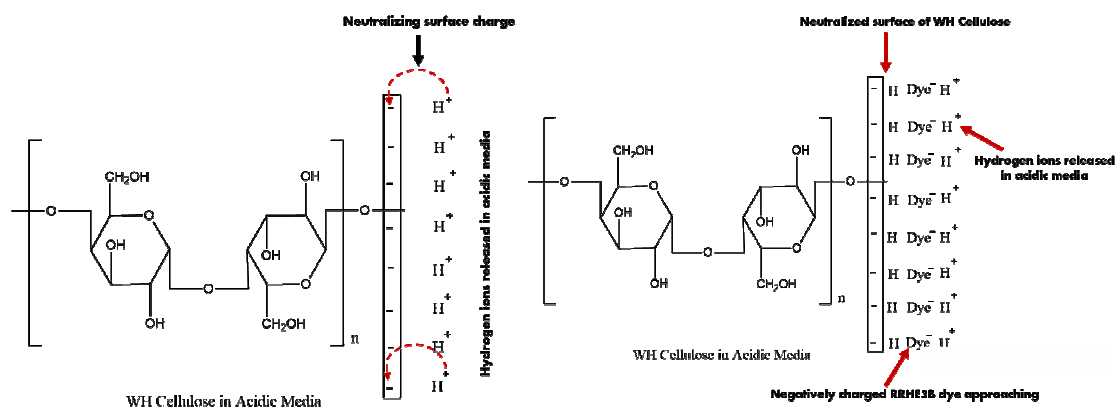


Figure 6: Adsorption mechanism of WH cellulose in acidic medium

### Effect of initial dye concentration

The effect of initial dye concentration on the adsorption of RR HE3B on the biosorbent was observed by varying it in the range from 25 to 100 mg/L, as shown in Figure 8. The removal of % RR HE3B dye exhibited a decrement with rising

initial dye concentration at pH 4 and pH 7, while at pH 10, an increment in the adsorption of the dye occurred. This may be explained by an enhancement of the interaction between RR HE3B dye and WH at alkaline pH.

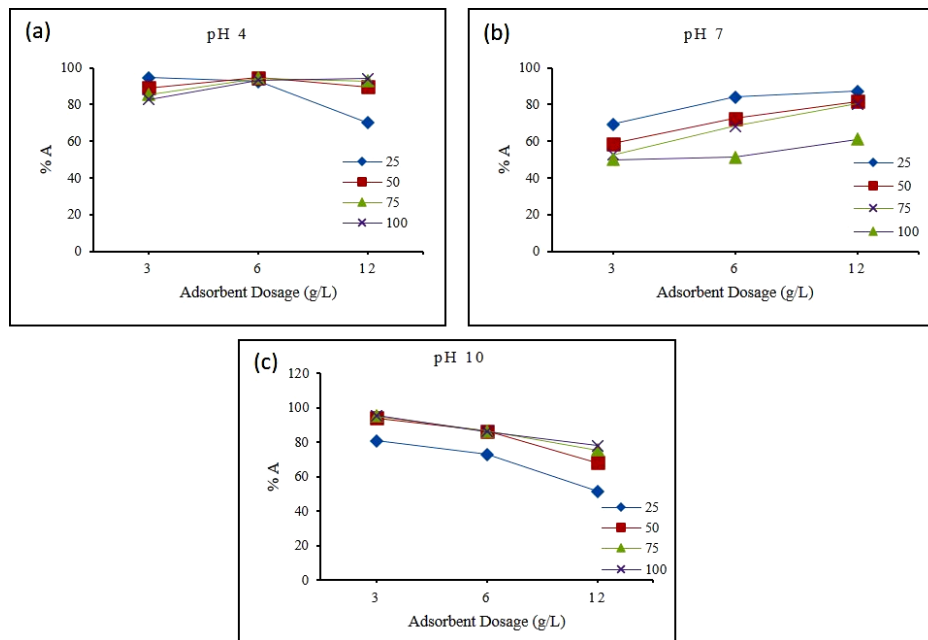


Figure 7: Effect of adsorbent dosage on adsorption capacity of WH towards RR HE3B at pH 4 (a), pH 7 (b) and pH 10 (c)

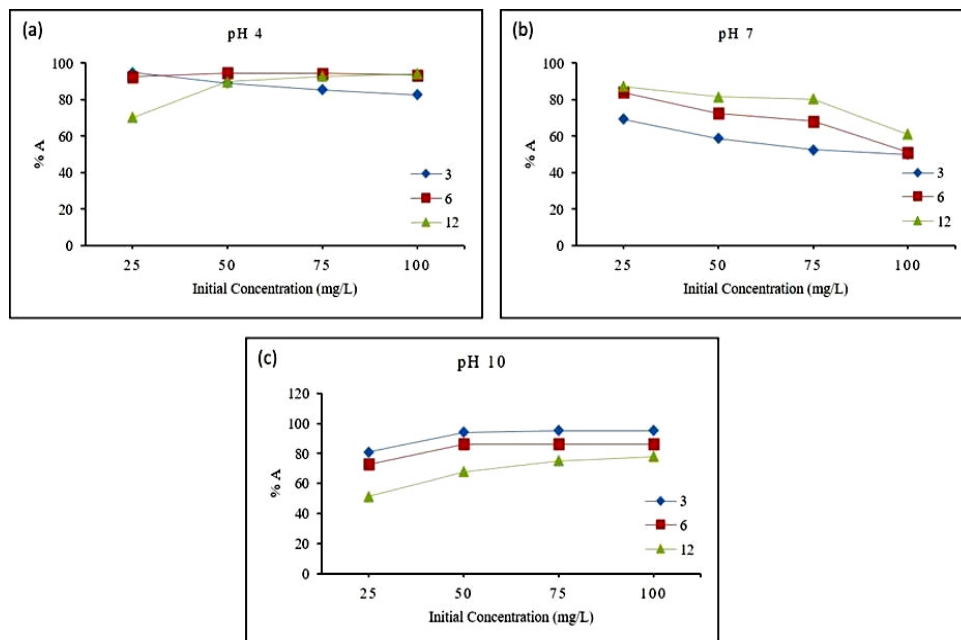


Figure 8: Effect of initial dye concentration on adsorption capacity of WH towards RR HE3B at pH 4 (a), pH 7 (b) and pH 10 (c)

### Adsorption equilibrium study

The adsorption capacity of the adsorbent at constant temperature is fundamental, and it is used widely in the determination of the maximum capacity of adsorption. It can also indicate how efficient is the adsorbent towards the adsorbate, and plays a significant role in determining how

economical would be the commercial application of the adsorbent for the specified solute. The study has considered the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models for the analysis of the experimental results. The plot between the amount of dye adsorbed onto WH and the equilibrium

concentration of the RR HE3B dye in the solution is shown in Figure 9.

**Langmuir isotherm model**

The Langmuir adsorption isotherm is based on the assumption that adsorption occurs through specific site attachment of the adsorbate to the adsorbent. The isotherm also assumes the absence of adsorbate molecules migration and the presence of constant adsorption energy. The linearized Langmuir adsorption has resulted in a 95.32% correlation coefficient, as shown in Figure 10. The Langmuir adsorption isotherm model can be expressed by Equation 2:<sup>20</sup>

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{2}$$

where  $q_e$  (mg/g) is the amount of dye retained by mass of adsorbent at equilibrium,  $C_e$  (mg/L) is the concentration of the dye at equilibrium,  $q_{max}$  (mg/g) is the maximum adsorption capacity of the adsorbent and  $K_L$  (L/mg) is the Langmuir constant that defines the energy constant related to the heat of adsorption.

**Freundlich isotherm model**

The Freundlich adsorption isotherm applies to adsorption onto non-homogeneous surfaces, while

interaction is confirmed between the adsorbed molecules. This model describes the exponential decrement of adsorption on completion of the sorption centers of the adsorbent. The linearized Freundlich adsorption has resulted in a 96.51% correlation coefficient, as shown in Figure 11. The Freundlich adsorption isotherm model could be expressed by Equation 3:<sup>21</sup>

$$q_e = K_f C_e^{1/n} \tag{3}$$

where  $q_e$  (mg/g) is the amount of dye retained by mass of adsorbent at equilibrium,  $C_e$  (mg/L) is the concentration of dye at equilibrium,  $K_f$  ( $\text{mg}^{(1-1/n)} \text{L}^{1/n} \text{g}^{-1}$ ) is the Freundlich constant representing the quantity of adsorbed dye per unit equilibrium concentration onto the adsorbent,  $n$  is a measure of the deviation from linearity of adsorption and  $1/n$  is the heterogeneity factor.

**Dubinin–Radushkevich isotherm model**

The Dubinin–Radushkevich adsorption isotherm model is used to differentiate whether the adsorption process is chemical or physical in nature. The linearized Dubinin–Radushkevich adsorption has resulted in 71.32% correlation coefficient, as shown in Figure 12.

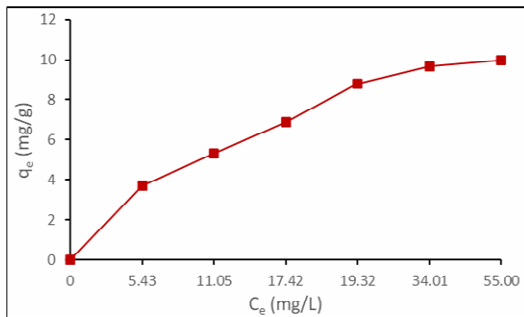


Figure 9: Amount of RR HE3B dye adsorbed onto WH ( $q_e$  vs.  $C_e$ )

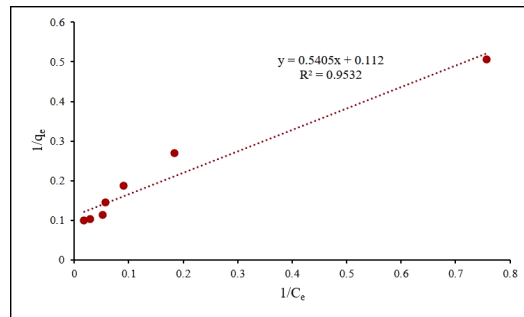


Figure 10: Linearized Langmuir adsorption isotherm

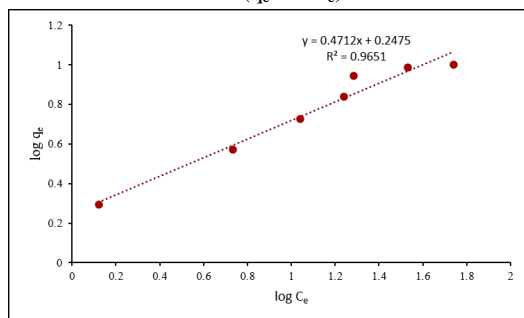


Figure 11: Linearized Freundlich adsorption isotherm

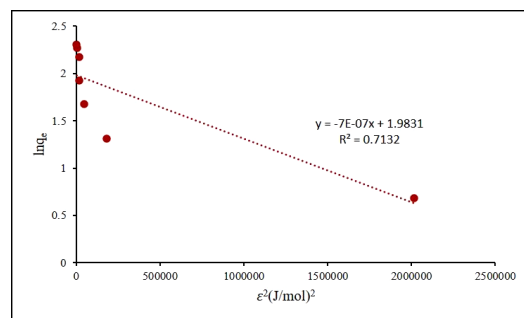


Figure 12: Linearized Dubinin-Radushkevich adsorption isotherm

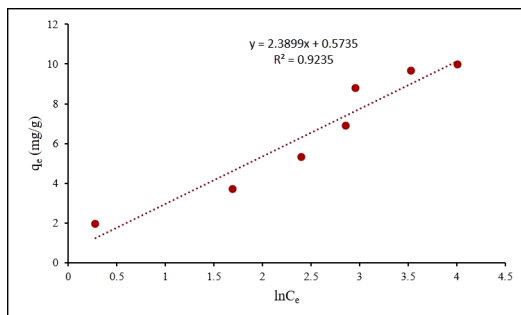


Figure 13: Linearized Temkin adsorption isotherm

It could be expressed by Equation 4:<sup>22</sup>

$$q_e = q_{max} e^{-\beta \varepsilon^2} \tag{4}$$

where  $q_e$  (mg/g) is the amount of dye retained by mass of adsorbent at equilibrium,  $q_{max}$  (mg/g) is the Dubinin–Radushkevich maximum monolayer adsorption capacity,  $\beta$  ( $\text{mol}^2/\text{KJ}^2$ ) is a constant related to sorption energy, and  $\varepsilon$  is the Polanyi potential expressed by Equation 5:

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \tag{5}$$

where  $R$  (8.314 J/mol K) is the gas constant and  $T$  (K) is the absolute temperature. The mean free energy ( $E$ ) of the system could be expressed by Equation 6:

$$E = \frac{1}{\sqrt{2\beta}} \tag{6}$$

**Temkin isotherm model**

The Temkin adsorption isotherm model explicitly takes into consideration the interaction of the adsorbent with the adsorbate. The model assumes the presence of a linear decrement of the heat of molecules with coverage due to the interaction between the adsorbent and the adsorbate; also, uniform distribution of binding energies is assumed. The fall in the heat of

sorption is linear, but not logarithmic, as in the case of the Freundlich adsorption model. The linearized Temkin adsorption equation has resulted in a 92.35% correlation coefficient, as shown in Figure 13. The Temkin adsorption isotherm model could be expressed by Equation 7:<sup>23</sup>

$$q_e = B \ln(AC_e) \tag{7}$$

where  $q_e$  (mg/g) is the amount of dye retained by mass of adsorbent at equilibrium,  $C_e$  (mg/L) is the concentration of the dye in the solution at equilibrium, while  $A$  and  $B$  are Temkin isotherm constants.

The experimental data were analyzed using Microsoft Excel. The experimental data yielded excellent fits in the following order: Freundlich ( $R^2 = 0.965$ ) > Langmuir ( $R^2 = 0.953$ ) > Temkin ( $R^2 = 0.9235$ ) > Dubinin-Radushkevich ( $R^2 = 0.7132$ ), based on the  $R^2$  values (Table 1). Based on the principle stated in a previous study,<sup>19</sup> it could be said that the physical adsorption process might be favored in this case, considering that the Freundlich constant ( $n$ ), which is a measure of deviation from the linearity of adsorption, has a value greater than unity.

Table 1  
Parametric values for each model

Isotherm model	Parameter	$R^2$
Langmuir	$q_{max} = 8.9286$	0.953
	$K_L = 0.2072$	
Freundlich	$K_F = 1.768$	0.965
	$n = 2.122$	
Temkin	$A = 0.5735$	0.9235
	$B = 2.3899$	
Dubinin-Radushkevich	$q_{max} = 7.265$	0.7132
	$\beta = -7 \times 10^{-7}$	
	$E = 845.154$	



The maximum monolayer adsorption capacity reported in several previous studies on dye removal using various adsorbents, in comparison with that obtained in the present work, is summarized in Table 2. The study by Tarawou *et al.*<sup>24</sup> has revealed that the surface area of water hyacinth quite high, with a value of  $102.6 \pm 3.58$

$\text{m}^2/\text{g}$ , while the pore size (22.85 nm), determined by Mukaratirwa-Muchanyereyi *et al.*,<sup>25</sup> and the surface functional groups might be additional reasons explaining the high monolayer adsorption capacity of the water hyacinth powder towards the Reactive Red HE3B dye.<sup>26</sup>

Table 2  
Maximum monolayer adsorption capacity of different adsorbents

Dye type	Adsorbent	$q_{\text{max}}$ (mg/g)	Reference
Reactive Red HE3B	WH powder	8.9286	Present work
Congo Red	Acid activated red mud	7.08	27
Congo Red	Activated carbon prepared from coir pith	6.70	28
Congo Red	Cashew nut shell	5.184	19
Methylene Blue	Walnut shell-AC	3.53	29
Methylene Blue	Almond shell-AC	1.33	30
Reactive Red 158	Acid activated <i>C. nucifera</i> L. shells	0.9728	18

## CONCLUSION

*Eichhornia crassipes* (WH) is an invasive plant, freely floating on rivers and lakes, its control is quite difficult and, because of its rapid proliferation, it poses serious threats to the biodiversity of ecosystems. Thus, developing an adsorbent from this biomass is expected to be an economically sound solution.

The results obtained from the FTIR analysis in the present study indicate that the WH can be a viable option as an alternative adsorbent for RR HE3B removal. The system removes RR HE3B dyes better at lower pH, but it also has a high removal capacity at higher pH values (pH 10). The adsorbent dosage has a significant impact on dye removal: at lower pH values, with an increasing dosage, the removal decreased, while at pH 10, as the dosage of the adsorbent was increased, the % removal of RR HE3B dye also increased. The increase in the initial dye concentration resulted in a decrease of %RR HE3B dye removal from the solution, while at pH 10 an increment was noticed. The adsorption isotherm data were analyzed using the Langmuir, Freundlich, Dubini-Radushkevich and Temkin isotherm models. The characteristic parameters for each isotherm model and related correlation coefficients have been computed. The experimental data yielded excellent fits in the following isotherm order: Freundlich > Langmuir > Temkin > Dubinin-Radushkevich, based on their correlation coefficient values.

To conclude, the water hyacinth can be considered as a potential alternative adsorbent for the removal of RR HE3B dye from aqueous

solutions. This approach would be useful especially in developing countries, for small and medium scale enterprises in dye effluent treatment, using stirred tanks, without mixing the solutions with other effluents.

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