REMOVAL OF MALACHITE GREEN FROM AQUEOUS SOLUTION BY SORPTION METHOD ON ALKALI-ACTIVATED WATER HYACINTH STEMS

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Abstract

Water hyacinth (*Eichhornia crassipes)* was found to have biosorption capacity for cationic dye, malachite green (MG) from aqueous solutions. The study was carried out under various experimental conditions such as dye concentration, adsorption dose, pH and temperature to assess the potentiality of alkali activated water hyacinth stems (AAWHS) for the removal of malachite green dye from waste-effluents. A high percentage of dye removal was observed with the decrease in the initial concentration of dye and increase in amount of adsorbent. Equilibrium isotherms were analysed according to the Langmuir models of adsorption, showing to be applicable with maximum monolayer adsorption capacity of 13.33 mg/g. The dimensionless factor, R_L of the malachite green dye, AAWHS isotherm revealed that the adsorption process is favorable in nature.

Keywords: adsorption, malachite green, adsorption isotherms, Water hyacinth stems.

1. Introduction

Dyes are important water pollutants which are generally present in the effluents of the textile, leather, food processing, dyeing, cosmetics, paper, and dye manufacturing industries. They are synthetic aromatic compounds which are embodied with various functional groups [1]. These coloured compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into the stream and reducing the photosynthetic reaction. Some dyes are also toxic and even carcinogenic. Therefore, it is highly necessary to reduce dye concentration in the wastewater [2]. The stability of dyes towards light and oxidizing agents also create a problem for their removal by different waste treatment procedures. Hence, their removal methods are selected with a great deal of care and thoughtfulness. Formerly, conventional method adopted by textile industries for removal of coloration from their disposed waste includes froth flotation, flocculation, coagulation etc. However, all such methods were found inefficacious and incompetent [3]. Some of the dyes and pigments present in these effluents resist biological oxidation and require tertiary treatment [4].Cytoplasmic azo reeducates

play an important role in the anaerobic biodegradation of azo dyes to produce colourless aromatic amines. Although complete mineralization is difficult, the resulting aromatic amines produced during anaerobic degradation may be toxic and carcinogenic. These amines are resistant to further anaerobic mineralization. During the last 10 years, the attention has been shifted towards adsorption technique, which has emerged as one of the widely accepted methods for the removal of all such contaminants [3]. Granular or powdered activated carbon is the most widely used adsorbent because it has an excellent adsorption capability for organic compounds, but its use may be limited due to its high cost [4]. This has led many workers to search for cheaper sources to prepare activated carbons or cheaper substitutes like fly ash, silica gel, wool wastes, blast furnace sludge, and clay materials (bentonite, kaolinite, montmorillonite, etc.). The ability of water hyacinth (*Eichornia crassipes*) to remove heavy metals in solution is well documented [5,6,7]. It was found that the metals were mostly concentrated at the roots of the plant and translocation appeared to be slow. This means that the root system could act as a biosorbent for various materials, which are soluble in water. This study also aimed to remove the dye malachite green from the aqueous solution using thermally activated water hyacinth roots as adsorbent and to study the effects of process variables like activation temperature, initial pH, sorbent dosage and initial dye concentration on the amount of dye uptake with equilibrium and kinetics of sorption mechanism.

## 2. Material and methods

2.1. Preparation of adsorbent

The water hyacinth used in this study was obtained from EL-Manzala leak, Dakahlia Governorate, Egypt. The collected biomaterial was extensively washed with tap water to remove soil and dust and sliced into pieces. The sliced material was dried by exposure to the sunlight for 7 days and subsequently at 60°C for 2 h in a hot air convection oven. The dried material was milled into a powder using 'domestic mixer' and was allowed to pass through a 20 to 80 mesh opening size sieve. For further studies the sieved powder was treated with 1.0 N NaOH for 24 h. After that, the samples were filtered and rinsed with distilled water .The treated material was dried again at 60°C for 2 h, sealed in plastic bags, and stored in desiccators for use.

2.2. Preparation of malachite green solution

The cationic dye malachite green (C.I. 42000) was obtained from Koch-Light Laboratories Ltd, England, and used without further purification. The dye stock

solution of 500 mg/L was prepared using distilled water. The experimental solution was prepared by diluting the stock solution with distilled water when necessary.

$$\overset{+}{N}(CH_3)_2\overset{-}{Cl}$$
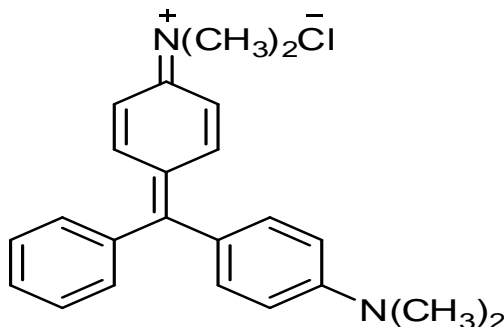
Chemical structure of malachite green dye (C.I. 42000)

2.3. Adsorption studies

In batch adsorption experiments, certain amounts of alkali-activated water hyacinth stems (AAWHS) were added into several 20 mL bottles, each containing 20mL solution of MG dye with an initial concentration of 20mg/L.Then the bottles were stirred at 450 rpm for 1 hr using a magnetic stirrer at $25^{\circ}C$ temperature. AAWHS in the samples was separated by filtration and the concentrations of the dye at a given time (C_t) were determined in the supernatant solutions. Adsorption isotherms were determined by introducing 0.02g (1.0g/L) AAWHS to respective 20 mL of different dye concentrations (10-80mg/L) at room temperature.

2.4. Effect of sorbent dosage

In order to find out the effect of sorbent dosage on the dye uptake a set of trials were carried out with AAWHS, whose dosage ranges from 0.5 to 3 g/L of aqueous dye solution throughout this set of experiments, dye concentration was maintained constant at 20 mg/L. After shaking, the samples were analyzed for color reduction in the UV spectrophotometer at λ_{max} 618 nm.

2.5. Effect of pH

The effect of pH on the dye uptake was studied by agitating 20 mg/L Malachite green solution with 0.02g of acid AAWHS in the pH range of 2- 12. The dye solutions were adjusted to the required initial pH values by adding HCl or NaOH.

2.6. Effect of initial dye concentration

AAWHS were shaken with 20 mL of aqueous dye solution whose concentration varied in the range of 10 to 80mg/L in several bottles. The bottles

were stirred for 1h at 450 rpm. Each bottle was filtered at the end of experiment and dye concentrations in samples were analyzed using UV spectrophotometer.

3. Result and discussions

3.1. Effect of contact time and concentration

The adsorbate concentration and contact time between adsorbent and adsorbate species play a significant role in the process of removal of pollutants from water and wastewater by adsorption at a particular temperature and pH. A rapid uptake of pollutants (dye) and establishment of equilibrium in a short period signifies the efficiency of the adsorbent for its use in wastewater treatment. In addition to this, the contact time is one of the factors for the development of surface charges at solid solution interface. The initial concentration of adsorbate also plays an important role as a given mass of the adsorbent can adsorb only a fixed amount of the solute. The more concentrated the solution or effluent, the smaller is the volume of effluent that a given mass of adsorbent can purify. Fig. 1 indicates the MG dye uptake as a function of contact time at temperature of 25°C. Fig. 1. shows that the rate of dye uptake by water hyacinth steams is quite rapid and maximum uptake occurred in the first 10 minutes for MG. This rapid rate of cationic dye uptake by water hyacinth stems has a significant importance for applications in small reactor volumes. Thus it gives economical and effective advantages.
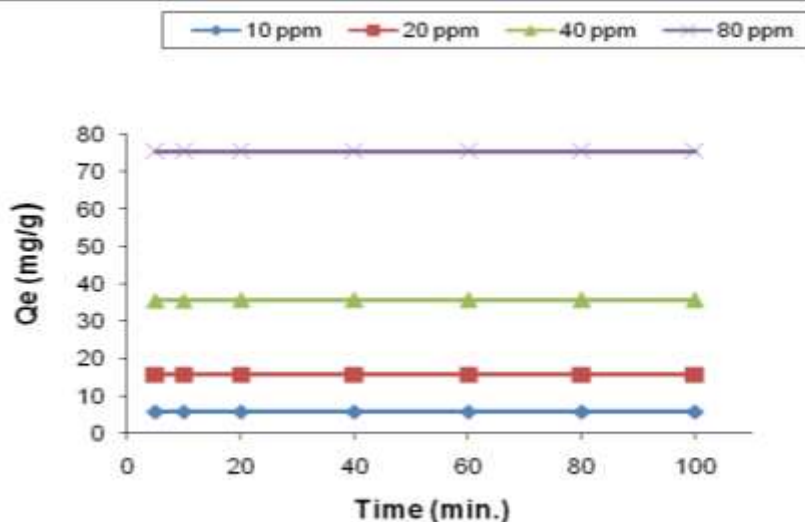

Fig. 1. Effect of concentration of MG by AAWHS (temperature $25\pm2^{\circ}$C; pH 9)

3.2. Effect of pH

Because initial pH of solution can significantly influence sorption of dyes, the effect of pH on dye sorption by the AAWHS was studied. The value of pH used ranged from 2 to 12.As elucidated in Fig. 2., the maximum dye uptake was at the initial pH 9. The dye adsorbed increased as the initial pH was increased from 2 to 9.When the pH varied from 9 to 12 the amount of dye adsorbed remained nearly constant. Previously, a number of studies have reported that there exist a linear relation between pH and the amount of dye (basic) adsorbed [8].At lower pH, the sorbent surface might have become negatively charged attracting more of the basic dye molecules. It is likely that charges develop on the surface of an adsorbent in an acidic medium, resulting in a higher adsorption of anionic dyes than in cationic dyes. If this is the case, the sorption of cationic dye should decrease at a lower pH [9]. As a result of this study, the optimal pH was shown to be 7.
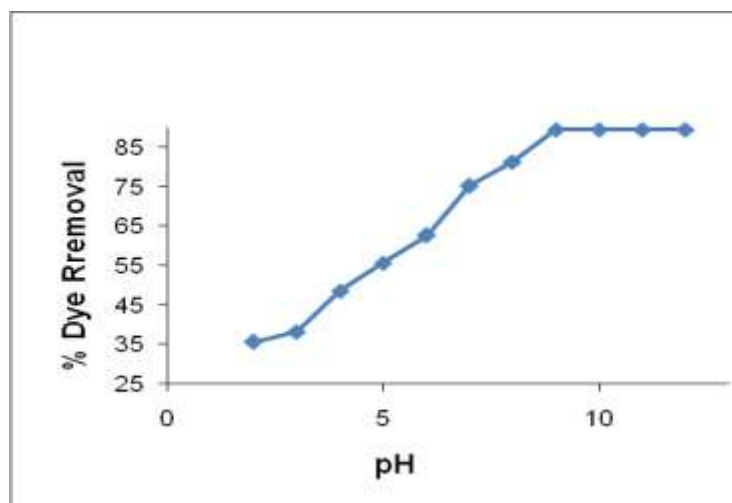

Fig. 2. Effect of pH on the removal of MG by AAWHS (concentration: 20 mg/L; temperature 25 ± 2°C)

3.3. Effect of sorbent concentration

The adsorption of the Malachite green dye on water hyacinth steams was studied by varying the carbon concentration (500-3000 mg/L) for 20 mg/L of dye concentration. The percent adsorption increased with increase in the carbon concentration (Fig. 3). This was attributed to the increased carbon surface area and availability of more adsorption sites [10,11]. Hence the entire studies were carried out with the adsorbent dose of 20 mg of adsorbent /20 ml of the adsorbate solution.
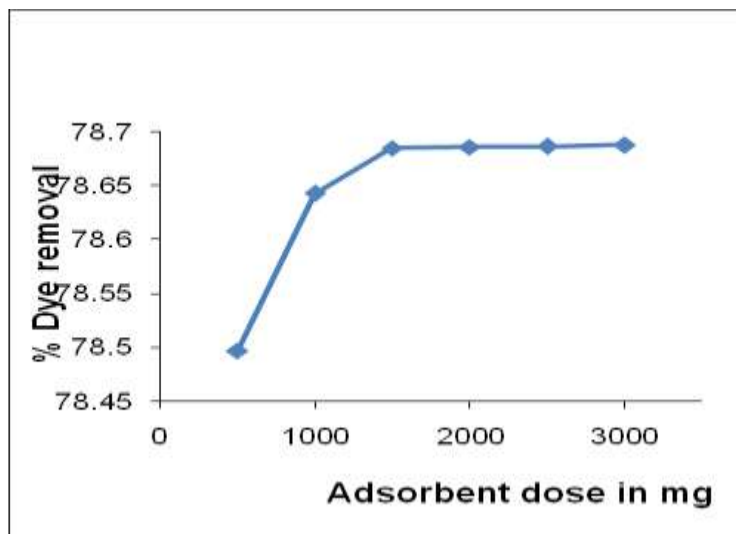
Fig. 3. Effect of adsorbent dose on the adsorption of MG by AAWHS
(concentration: 20 mg/L; temperature $25 \pm 2^{o}C$)

3.4. Effect of particle size

The particle size of the adsorbent has significant influence on the kinetics of adsorption. The influence of particle size furnishes important information for achieving optimum utilization of adsorbent and on the nature of breakthrough curves. Rate of adsorption on a solid surface are expected to vary with available surface area for a constant adsorbent masses with the particle size. The adsorption capacity is directly proportional to the total exposed surface and inversely proportional to the particle diameter for non-porous adsorbent. The presence of a large number of smaller particles provides the adsorption system with a greater surface area available for the dye removal [12].The result of contact time investigation using several particle size ranges of adsorbent were analysed. It is observed that as the particle size decreased the amount of adsorbed dye increased. This is due to the larger external surface area available due to smaller particle, when the total mass of the adsorbent is constant [13]. It is evident from Fig. 4. that the adsorption of malachite green from a solution of concentration 20 mg/L is found to increase from 78.5 % to 79 % with a decrease in the particle size of the adsorbent (water hyacinth steams) from 20-30 mesh to 40-80 mesh at $25 \pm 1^{o}C$ and pH 9.
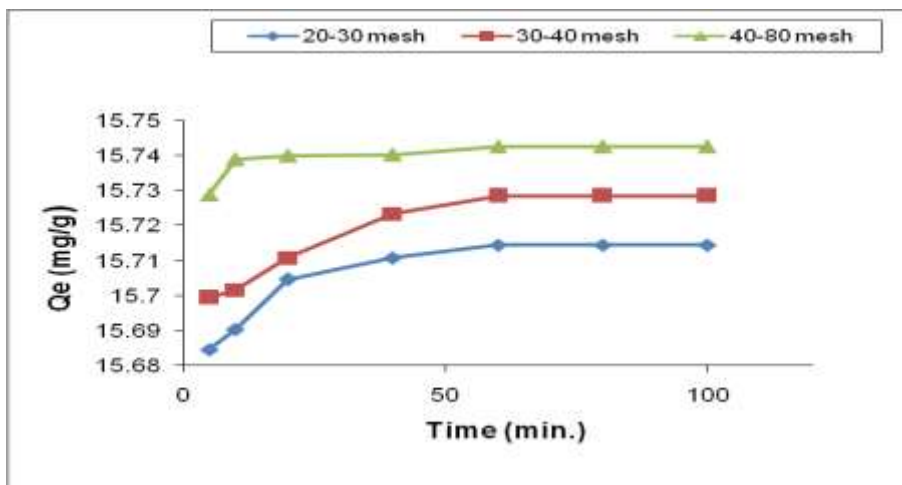
Fig. 4. Effect of particle size of AAWHS on the removal of MG (concentration: 20 mg/L; temperature 25 ± 2°C)

3.5. Effect of temperature

The adsorption rate constant of the removal of malachite green with initial concentration of 20 mg/L at pH 9 on alkali activated water hyacinth steams has been determined. Thermodynamic parameters such as change in free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) at temperatures 25,35 and 45°C have been evaluated to explain the results.

The result of time rate studies for the adsorption of malachite green at different temperatures are given in table 1.

Table 1. Effect of temperature on the removal of malachite green dye on AAWHS(initial concentration of the dye: 20mg/L).

Temperature (^{o}C)	Amount adsorbed (mg/g)	% removal
25.0	15.72	78.7
35.0	15.70	78.5
45.0	15.6	78.4

The removal of malachite green decreased from 78.7% to 78.4% by alkali activated water hyacinth steams with an increase in temperature from 25°C to 45°C at 20 mg/L concentration of the dye shown in fig. 5, which is indicative of exothermic nature of the process. This can arise due to a tendency of the dye

molecules to escape from the solid phase to the bulk solution with an increase in temperature of solution [14].

The variation in the extent of adsorption with temperature may be explained on the basis of the change in chemical potentials [15] which is related to the solubility of the adsorbate species, being increased with an increase in the temperature. The adsorption reaction at any interface between two phases can be regarded as an equilibrium process; the point of equilibrium is being dictated by the relative energies. These energies values can be defined in terms of different thermodynamic parameters such as standard free energy, enthalpy and entropy changes for adsorption which have been calculated using the standard procedures.

The negative value of ΔG^O is indicative of a spontaneous process with a high affinity of the surface of the used adsorbent to such type of dyes. Further, the negative values of enthalpy and entropy changes suggest the exothermic nature of adsorption and randomness of the system. The calculated values for ΔG^O, ΔH^O and ΔS^O are given in table 2.

Table 2: Thermodynamic parameters for the dye MG on AAWHS

Temperature (^{O}C)	Thermodynamic parameters		
	$-\Delta G^O$(KJmol^{-1})	$-\Delta H^O$ (KJmol^{-1})	$-\Delta S^O$(JK^{-1}mol^{-1})
25.0	6.41	9.29	9.85
35.0	6.37	7.22	6.14
45.0	6.22	4.51	3.26

3.6. Adsorption isotherm

To study the adsorption isotherm, 0.02 g of the adsorbent (AAWHS) was taken with 20 ml of an aqueous solution of the dye at different concentrations (10-80 mg/L) in a water bath until the equilibrium is established in each bottle. The experiments were carried out at 25, 35 and 45°C. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of surface. The experimental data for the uptake of the dye malachite green by adsorbent (AAWHS) have been correlated with the rearranged Langmuir´s model of adsorption in the present investigation:

$$Ce/qe = Ce/Qo + 1/Qob$$

Where C_e is the equilibrium concentration (mg/L) of the dye, q_e is the amount (mg/g) of the dye adsorbed at equilibrium and Q^O and b are the Langmuir constants related to adsorption capacity and energy of the adsorption, respectively. The plot of C_e / q_e versus C_e at different temperatures for the MG (Fig. 5) is found to be linear, suggesting the applicability of Langmuir isotherm.
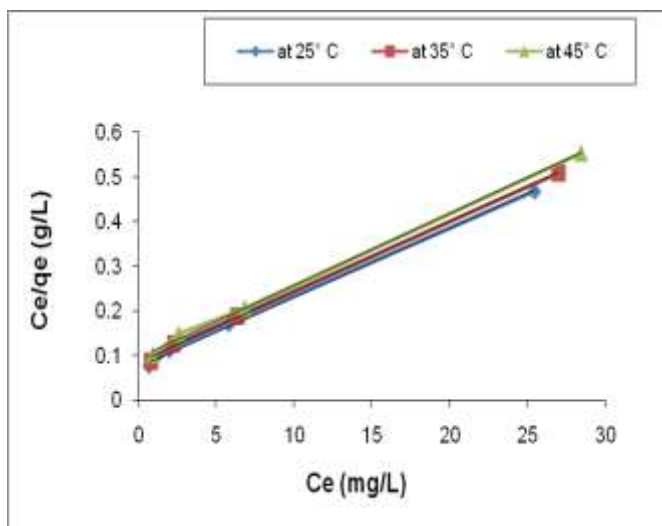

Fig. 5. Langmuir plot for the adsorption of MG on AAWHS at different temperatures.

The values of Q^O and b at different temperatures were determined from the slopes and intercepts of the respective plots and are presented in Table 3. It is evident from Table 3 that the amount of of malachite green adsorbed (Q^O) by AAWHS varies from 13.33 to 10.52 mg/g, with the increase of temperature from 25 to 45°C.

Table 3. Langmuir constants for the dye MG on AAWHS

Temperature (^{o}C)	Langmuir constants		
	Q^O (mg/g)	b (L/mg)	R_L
25.0	13.33	0.21	0.741
35.0	12.04	0.18	0.821
45.0	10.52	0.16	0.854

The essential characteristics of a Langmuir isotherm can be described by a separation factor or equilibrium parameters R_L which is defined by

$$R_L = 1/(1 + bCo)$$

Where C_o is the critical concentration (mg/L) and b is the Langmuir constant. The value of R_L for the adsorption of MG on AAWHS indicates that the adsorption process is very favourable because R_L value lies between 0 and 1 (Table 3).

4. Conclusion

Alkali activated water hyacinth stems (AAWHS) shows significant adsorption capacity for Malachite Green (MG) dye under suitable experiment conditions and hence will serve as an useful adsorbent. The water hyacinth are abundantly available and are inexpensive too. Its binding capacity to basic dyes is appreciably high. The method may be helpful for designing and fabricating basic dye rich effluent treatment plant in the future.

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