Sorption of malachite green and Rhodamine-B dyes from aqueous solution by biomass waste: Kinetics, isotherm and thermodynamic studies

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A biomass waste has been evaluated without chemical modification as low-cost effective adsorbent to remove Malachite Green (MG) and Rhodamine-B (RhB) dye srespectively from aqueous solution in batch experiment. The effect of certain parameters on the adsorption capacity has been investigated such as particle size, contact time, initial dye concentration, pH, mass of the adsorbent and the effect of temperature. Isotherms study has been described by the Freundlich model which indicates that MG and Rh-B sorption process onto biomass is more described by good correlation coefficients (R^2=0.867 and 0.953, respectively). Kinetic study shows that MG and Rh-B adsorption process follow pseudo-second order kinetics model. Furthermore, thermodynamic parameters reveal that the adsorption is spontaneous and endothermic.

Keywords: Biomass waste, Dyestuffs, Batch system, Sorption

Industrial processes generate wastewaters containing organic pollutants with negative impacts on humans and environment. These pollutants include dyes, which are used by many industries to color their products. Textile dyes, even in trace amounts, are a major environmental problem. They generate consequently a considerable number of coloured wastewaters which reduce light penetration, have a derogatory effect on photosynthesis and are also potentially toxic/carcinogenic because of the complexity of their chemical structures and especially their low biodegradability[1,2]. Various techniques have been employed for the removal of dyes from wastewaters such as nanofiltration, coagulation, floculation, biodegradation, ozonation, oxidation, membrane separation and biological process[3]. Adsorption is a physico-chemical process that offers an economical and effective technology. Activated carbon is the most effective, popular and commonly used adsorbent (powder or granular form) because of its large surface area, microporous structure, high adsorption capacity[4] but its widespread use is restricted due to its high cost; moreover, its regeneration and reuse makes it more costly.

Therefore, extensive investigations are being carried out to identify other sorbents. Recent research focused on the effectiveness of low cost adsorbents. For this purpose, biomaterials which are bioproducts or agricultural and industrial by-product wastes have been proposed as economic and eco-friendly adsorbents[5]. Investigation into the use of waste as low-cost adsorbent, especially bioresource materials as an alternative adsorbent give economical advantage, encourage waste management and aid environmental protection. Previously, several studies have shown that biomass such as chitin, coffee, tea waste and rice husk can be used as alternative low-cost adsorbents[6-11]. In Algeria, about 25.000 tonnes of apricot stones per year are produced[12]. Apricot stone is considered as a cheap precursor for activated carbon source. Therefore, it is important to evaluate its performance as adsorbent[13].

The aim of the present work is the evaluation of agricultural solid waste available freely locally, the apricot kernel shell, without chemical modification as low-cost effective adsorbent to remove Malachite Green (MG) and Rhodamine-B (RhB) dyes respectively from aqueous solution in batch

experiment. Isotherm, kinetic and thermodynamic studies were investigated.

Experimental Section

Adsorbent

The starting material was Apricot Kernels Shell (AKS) (an Agri- food wastes) provided from Producer Company of apricot juices in the region of N'Gaous west of the Aures (Batna, Algeria). This material underwent a purification stage. The shells were washed with distilled water several times to remove the dirt and dust and oven-dried at 105°C for 24 h. It was ground, sieved to different sizes and then stored in covered glass containers for further uses without any further chemical or physical treatment before adsorption experiments. The ash content, moisture content, and pH of the apricot kernel shell were estimated using standard methods[14]. The pH at the point of zero charge (pH_{PZC}) of the raw biomass, i.e. the pH for with the surface charge is zero (Table 1), is determined using mass titration[15].

Adsorbates

Malachite Green (MG) (CI name: Basic green 4 (BG4), chemical formula $C_{23}H_{25}N_2Cl$, molecular weight 364 g.mole^{-1}) and Rhodamine B(Rh-B) (CI name: Basic violet 10; Chemical formula: $C_{28}H_{31}N_2O_3Cl$; Molecular weight 479 g.mole^{-1}). The appropriate wavelengths of MG and Rh-B were obtained using the Spectrophotometer model Shimadzu 170 UV/visible. The chemical structure of MG and Rh-B are shown in Figs. 1 and 2. Dye stock solutions (1000 mg.L^{-1}) were prepared by dissolving appropriate amount of dye powder into brown flasks in distilled water. By diluting the dye stock solutions with distilled water, the solutions at required concentration were adjusted for sorption experiments.Working dyes solutions (stock and diluted solutions of 10 mg.L^{-1} of MG and RB) were then kept in brown flasks at room temperature in the dark to prevent any possible dye photodegradation.

Batch experiment

Experiments were carried out in 250 mL brown glass erlenmeyer flasks containing 100 mL of dye solution (MG solution and Rh-B solution separatly).

An appropriate amount of biomass was added to the dye solution. The flasks were shaken at a constant speed of 200 rpm on a horizontal shaker (EDMUND BÜHLER GMBH SM-30). After adsorption, the samples were filtered with Wathman filter paper and the filtrate was analysed for the residual dye concentration of MG or Rh-B using UV-spectrophotometer (Shimadzu, Model UV 1800,) at $\lambda_{max} = 618$ nm and $\lambda_{max} = 553$ nm, respectively.

The amount of dye adsorbed at equilibrium, Q_e (mg.g^{-1}) was calculated using the following equation (Equation 1):

$$Q_e = (C_0-C_e) \times V/m \qquad ... (1)$$

where C_0 and C_e (mg.L^{-1}) are the concentration of dye at intial and equilibrium, respectively. V(L) , is the volume of solution and W(g) is the mass of dry sorbent used. The percentage removal is calculated using Equation 2:

$$R \% = (C_0 - C_e)/C_0 \times 100\% \qquad ... (2)$$

The effect of various parameters such as adsorbent particles sizes: $d_1 < 0.1$ mm, $0.1 < d_2 < 0.2$ mm, $0.2 < d_3 < 0.4$ mm, $0.4 < d_4 < 0.65$ mm, pH (02-11), intial dye concentration (10-80 mg.L^{-1}), contact time (0-120 min) and adsorption temperature (20,40,60 and 80°C) were investigated.

Results and Discussion

Batch adsorption

Effect of biosorbent particles size

In this study, the effect of biosorbent particle size on the MG and Rh-B adsorption was studied within
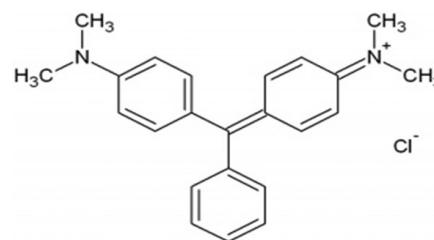

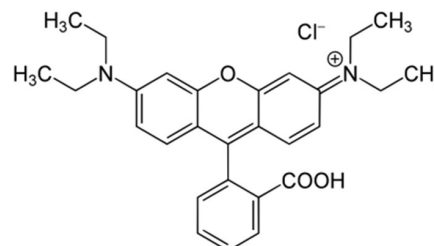Fig. 1 — Chemical structure of Malachite green (MG).

Fig. 2 — Chemical structure of Rhodamine-B (Rh-B).

Table 1 — Characteristics of the adsorbent

Moisture content (%)	7.9 ± 0.1
Ash content (%)	15.9 ± 0.1
Volumetric mass (g.cm^{-3})	0.452 ± 0.1
Porosity	0.67 ± 0.1
pH_{Pzc}	7 ± 0.1

size range of $d_1 < 0.1$ mm, $0.1 < d_2 < 0.2$ mm, $0.2 < d_3 < 0.4$ mm, $0.4 < d_4 < 0.65$ mm (Fig. 3) in order to determine the optimum diameter for MG and Rh-B dyes adsorption. The initial dye concentration, adsorbent dose and temperature were fixed at 50 mg.L^{-1}, 0.5 g.L^{-1} and 293°K, respectively. Results have shown that better adsorption was observed with lower particle size (diameter lower than 0.1 mm). Smaller particles sizes give large surface area, which ensuing a high capacity and removal adsorption. Subsequently, d<0.1 mm was used in all adsorption experiments.

Effect of pH

The pH of the solution influence significantly on adsorption process, it determines the surface charge of adsorbent and the state of adsorbent. In this study, the effect of the solution pH on the MG and Rh-B adsorption onto ASC biomass was investigated while the initial dye concentration, adsorbent dose, contact time and temperature were fixed at 50 mg.L^{-1}, 0.5 g.L^{1}, 80 mn and 293°K, respectively. Dye molecules mainly interact with the adsorbent by electrostatic interaction, hydrophobic-hydrophobic interaction and hydrogen bonding[16]. As shown in Fig. 4, the equilibrium sorption capacity for MG and Rh-B within pH range 2-12 was different. For MG, the amount adsorbed of dye at equilibrium was minimum at pH 2, increased up to pH 8 and reached the maximum at pH 12. The point of zero charge (pH$_{pzc}$) is defined as the solution pH at which the net surface charge of the adsorbent particle is zero. The Knowledge of pH$_{PZC}$ permits to visualize the ionization of functional groups and their interaction with dyes solutions[16]. The pH$_{pzc}$ of ASC biomass was determined to be at 7. At solution pH higher than pH$_{pzc}$, then the adsorbent surface is negatively charged, enhancing the adsorption of MG, positively charged dye cation through electrostatic attraction. Similar results were reported for the adsorption of MG onto rattan saw dust[12], hydrilla Verticillata biomass[4]. The effect of the solution pH on Rh-B equilibrium sorption capacity has shown a higher sorption in the pH range of 2 to 4. Rh-B changes its acidity or basicity with a change in pH. Below pH 4.2, the Rh-B molecules are positively charged and the carboxylic group is neutral; while, at pH above 4.2, the Rh-B exists in zwitterionic form. Previously studies[4,17] have been reported that optimum adsorption of Rh-B was at pH of 3.

Effect of contact time and initial dye concentration

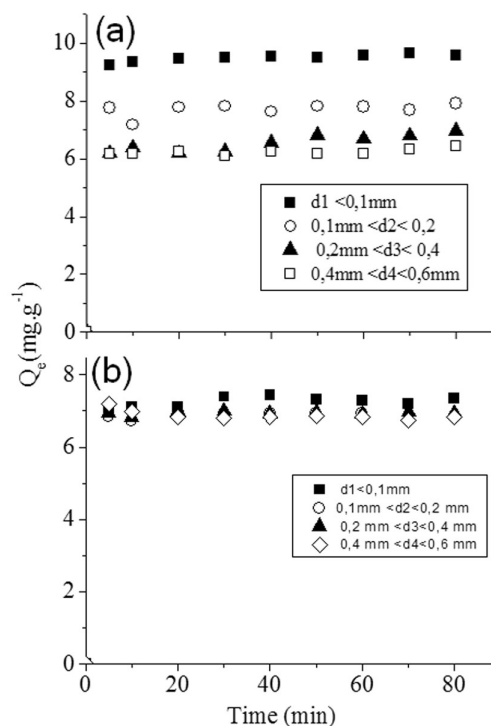The effect of contact time on the sorption of MG and Rh-B was studied for various initial dye

Fig. 3 — Effect of particles size on the biosorption of MG (a) and Rh-B (b) (temperature = 273°K, C_0= 50 mg.L^{-1}, shaking speed = 250 rpm, contact time = 60 min).
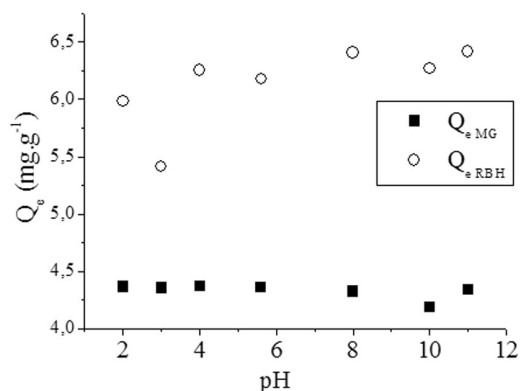

Fig. 4 — Effect of pH on the biosorption of MG and Rh-B (temperature = 273°K, C_0= 50 mg.L^{-1}, shaking speed = 250 rpm, contact time = 60 min).

concentrations. As shown in Fig. 5, the adsorption capacity of the biosorbent at different initial concentrations increased rapidly in the initial stage of contact period and equilibrium was reached in 40 min. The rapid adsorption of dyes may be attributed to the availability of active sites on the surface of biosorbent[18]. In addition, increases of equilibrium sorption capacity of biomass increase with increasing initial dye concentration. This is attributed to an increase in the driving force of the concentration gradient, as an increase in the initial dye

concentration[19]. The effect of the initial dye concentration factor depends on the immediate relation between the dye concentration and the available binding sites on an adsorbent surface[20].

Biosorption isotherms

Biosorption isotherms were investigated using three isotherms models, Freundlich, Langmuir and Temkin for determination of adsorption equilibrium characteristics of this biosorption process. Langmuir model is the adsorbate molecules adsorbed only one layer on the adsorbent. It assumes a homogeneous type of sorption[21]. Further, Freundlich model describes adsorption onto heterogeneous surface[22]. According to the Temkin isotherm[23], the adsorption heat of the molecules on the layer decreases with the
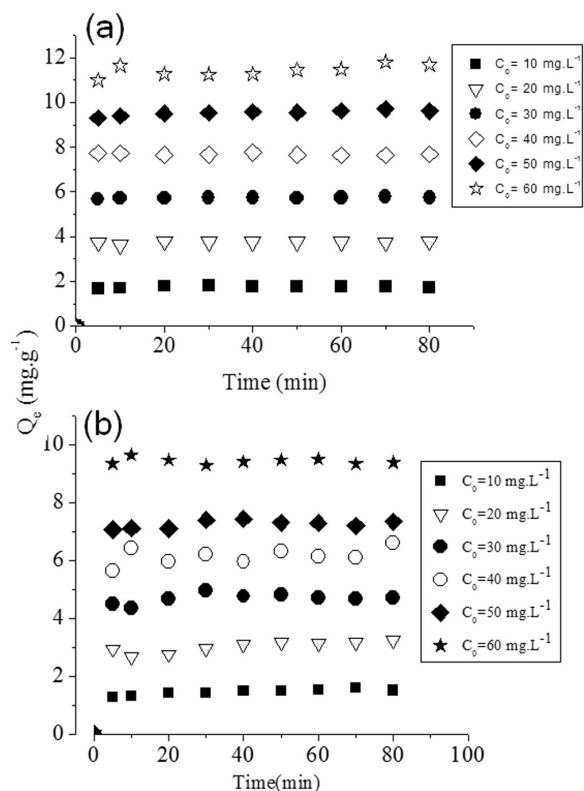

Fig. 5 — Effect of contact time and initial dye concentration on the biosorption of MG (a) and Rh-B (b) (temperature = 273°K, C_0= 50 mg.L^{-1}, shaking speed = 250 rpm,).

coverage linearly; because of adsorbent-adsorbate interactions.

The Freundlich equation is expressed as Equation 3:

$$\text{Ln } Q_e = \ln k_f + (1/n) \ln C \qquad ... (3)$$

where K_f (L.g^{-1}) and n are the freundlich constant, Qe (mg.g-1) is the corresponding adsorption at equilibrium and Ce (mg.L^{-1}) is the concentration of the MG and Rh-B at equilibrium (mg.L^{-1}).

The Langmuir equation is presented as Equation 4:

$$Ce/Qe = Ce/Qm + 1/Qm\,K \qquad ... (4)$$

where Qm (mg.g^{-1}) is the maximum adsorption capacity and K_L (L.mg^{-1}) is the Langmuir constant.

The Temkin equation is given by Equation 5:

$$Qe = B \ln (ACe) \qquad … (5)$$

where A is the Temkin isotherm energy constant (L.g^{-1}) and B is the Temkin constant.

In the present study, the adsorption of MG and RB by ASC is best described by Freundlich isotherm model. The regression coefficients (R^2) of the Freundlich model were 0.867 for MG and 0.953 for Rh-B, which were higher than coefficient of regression of the Langmuir model and Temkin model (Table 2). This indicates that the process sorption of MG and Rh-B onto AKS biomass was more described by Freundlich-model, determining the multilayer adsorption behaviour of the adsorbent-adsorbate system.

Biosorption kinetics

In order to investigate the adsorption processes of MG and Rh-B on AKS biomass, the pseudo-first order, pseudo-second-order and intra-particle diffusion models were used to test experimental data.

The pseudo-first order equation is expressed by Equation 6:

$$Q_t = Q_e\,(1-e^{-K_1}t) \qquad ... (6)$$

The pseudo-second order equation could be represented by Equation 7:

Table 2 — Freundlich, Langmuir and Temkin isotherm model parameters for MG and Rh-B biosorption by AKS biomass.

	Freundlich			Langmuir			Temkin		
	K_f (mg^{1-n} L^{n}g^{-1})	N	R^2	Q_{max}(mg.g^1)	K_L(L.g^1)	R^2	B	A(L.g^1)	R^2
MG	9.0993	0.613	0.867	91.39	0.072	0.82	12.655	9.94	0.740
Rh-B	0.0124	3.559	0.953	271.65	0.016	0.58	-33.06	30.47	0.535

Table 3 — Kinetic model for MG and Rh-B biosorption by AKS biomass

	Pseudo-first order kinetic model			Pseudo-second order kinetic model			Intra-particle diffusion		
	Q_e	K_1	R^2	Q_e	K_2	R^2	C	K	R^2
MG	9.523	2.862	0.989	3.097	6.338	0.999	9.422	0.052	0.758
Rh(b)	7.482	0.556	0.980	2.763	0.581	0.999	6.821	0.182	0.891

$$Q_t = Q_e [1-1/(Q_e K_2 t+1)] \quad \text{... (7)}$$

Intra-particle diffusion model

Diffusion mechanism of adsorption was studied evaluated using the intraparticle diffusion model[24] based on the theory proposed by Weber and Morris. During the intraparticle diffusion process, the adsorbents are most probably transferred from the bulk of the solution into the solid phase[25].

The intraparticle diffusion equation is represented by Eq. 8:

$$Q_t = K_{diff} t^{0.5} + C \quad \text{... (8)}$$

where Q_t (mg.g^{-1}) is the amount of dye adsorbed, K_{diff} (mg.g^{-1}.min$^{-0,5}$) is the intraparticle diffusion rate constant and C (mg.g^{-1}) is the intercept related to the thickness of the boundary layer. A large intercept suggests a great boundary layer effect[6]. The fitting of the experimental kinetics results and the values of the estimated parameters are presented in Table 3. The pseudo second-order kinetic model gives the best correlation for the biosorption process of MG and Rh-B.

Biosorption thermodynamics

Thermodynamic parameters relating to the adsorption process, the free energy change (ΔG, Kj.mol^{-1}), enthalpy change (ΔH, j.mol^{-1}) and entropy change (ΔS, j.mol^{-1}), were calculated using the following equations:

$$\Delta G = -RT \ln K \quad \text{... (9)}$$

$$\Delta G = \Delta H - T \Delta S \quad \text{... (10)}$$

where R is the universal gas constant (8.314 J.K^{-1}mol^{-1}), T the absolute temperature (°K)

and K is the equilibrium constant[13].Values of the thermodynamic parameters are shown in Table 4.

The values of the free energy change (ΔG) were negative, indicating the spontaneity of the adsorption process. The positive value of ΔS for AKS indicates the increased randomness in the system of the solid/solution interface during the adsorption of MG

Table 4 — Thermodynamics values of MG and Rh-B biosorption on AKS biomass

Adsorbate	ΔH J.mol^{-1}	ΔS J.mol^{-1}.K^{-1}	ΔG KJ.mol^{-1}			
			293°K	313°K	333°K	353°K
MG	5.78	48.64	-14.24	- 15.22	-16.19	-17.16
Rh-B	3.7	22.98	- 6.73	- 7.19	-7.65	- 8.11

and Rh-B. Further, the positive value of ΔH confirmed that the sorption on a biosourced material of MG and Rh-B is endothermic process.

Conclusion

The present study shows that the apricot kernels shell are effective and inexpensive biosorbents for the removal of MG and Rh-B dyes from aqueous solutions with percentage removal of 95.95% and 73.45%, respectively. The applicability of the Freundlich model indicates that MG and Rh-B sorption process onto biomass is more described by good correlation coefficients (R^2=0.867 and 0.953 , respectively). The kinetics studies show that MG and Rh-B adsorption process follow pseudo-second order kinetics model. Furthermore, the thermodynamic study reveal that the adsorption is spontaneous and endothermic.

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