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EQUILIBRIUM STUDY REGARDING CRYSTAL VIOLET DYE ADSORPTION ON RASPBERRY LEAVES POWDER

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ABSTRACT

This work focuses on the crystal violet removal from aqueous solution using raspberry leaves powder as adsorbent materials. SEM and colour analyses were used to characterize the adsorbent surface. The influence of pH, adsorbent dose and initial dye concentration was studied. Equilibrium modeling was performed to characterize the adsorption process and to determine the maximum adsorption capacity. Sips isotherm characterizes the adsorption and the maximum adsorption capacity, 264.5 (mg/g) was better compared with other similar adsorbents. The obtained results indicate that adsorbent material, obtained from raspberry leaves, is very suitable to be used for crystal violet removal from aqueous solutions.

KEYWORDS: dye adsorption, crystal violet, raspberry leaves, equilibrium isotherms

1. Introduction

Dyes are a major class of compounds that, once in the environment, can cause environmental imbalances. The main sources of dye pollution are wastewater from the textile, cosmetics, food, pharmaceuticals, paper and printing industries. If they are not treated properly, their discharge into natural effluents can have negative effects on aquatic fauna and flora [1-4].

Crystal violet is a dye with many industrial applications and also, in veterinary medicine. It has a toxic, carcinogenic and mutagenic potential on human health and the environment [3, 5, 6].

Various methods have been studied and applied to remove this dye from water such as: photo-catalytic degradation, membrane separation, catalytic reduction, chemical electrochemical oxidation, adsorption, microorganism degradation and biological treatment [2, 4, 6-8].

Adsorption is a preferred applied method in many cases because it is easy to operate, it has a good applicability and flexibility, high efficiency and relatively low costs [1-4, 8].

The use of cheap and available in large quantities adsorbent materials can make this process extremely cost-effective from an economic point of view [2-4].

This category includes vegetable waste such as: various seeds, leaves, steams, peels and husks [1-5, 8, 9].

Raspberry (*Rubus idaeus*) is a shrub that grows spontaneously or is widely grown in temperate areas of Europe, Asia and North America. Its fruits are appreciated for their taste and contain high amounts of vitamins, minerals, organic acids, tannins and flavonoids. These characteristics make raspberries to be used in the food, cosmetics and pharmaceutical industries [10-12]. The leaves of this shrub are available in large quantities in nature and have low cost.

The main aim of this study was to use this vegetable product to remove the crystal violet from aqueous solutions. Obtaining the adsorbent material from the raspberry leaves required minimal processing, without using chemical reagents and without heat treatment. Equilibrium modeling was performed to characterize the adsorption process and to determine the maximum adsorption capacity. It was compared with those obtained for other similar adsorbent materials used to remove the crystal violet dye from water.

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2. Experimental

The dried raspberry leaves were purchased from StefMar, Ramnicu Valcea. The adsorbent obtaining process (which involves grinding and washing) has been described in detail elsewhere [13].

To characterize the adsorbent surface, SEM and color analyzes were performed using a Quanta FEG 250 microscope and a Cary-Varian 300 Bio UV-VIS colorimeter (D65 illuminant), respectively.

All experiments were performed in three independent replicates, at constant mixing intensity. The pH was adjusted with NaOH (0.1 N) and HCl (0.1 N) solutions and the crystal violet concentration was determined using a UV-VIS spectrophotometer (Specord 200 PLUS) at 590 nm.

The adsorption capacity at equilibrium, (qe), was calculated with equation (1):

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

where: C_0 represents the initial crystal violet concentration (mg/L); C_e represents the crystal violet equilibrium concentration (mg/L); V represents the solution volume (L) and m represents the mass of adsorbent (g).

Langmuir, Freundlich, Temkin and Sips isotherms in the non-linear forms (equations 2-5) were used to analyse the adsorption equilibrium.

Langmuir isotherm equation:

$$q_e = \frac{q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (2)$$

Freundlich isotherm equation:

$$q_e = K_F \cdot C_e^{1/n_F} \quad (3)$$

Temkin isotherm equation:

$$q_e = \frac{R \cdot T}{b} \cdot \ln(K_T \cdot C_e) \quad (4)$$

Sips isotherm equation:

$$q_e = \frac{Q_{sat} \cdot K_S \cdot C_e^n}{1 + K_S \cdot C_e^n} \quad (5)$$

where: q_m and Q_{sat} represents the maximum absorption capacities; K_L represents the Langmuir constant, K_F represents the Freundlich constant, K_T represents the Temkin constant, K_S represents the Sips constant; $1/n_F$ represents an empirical constant indicating the intensity of adsorption; R represents the universal gas constant; T represents the absolute temperature; b represents Temkin constant which related to the adsorption heat and n represents Sips isotherm exponent [14-16].

3. Results and Discussion

3.1. Adsorbent surface characterization

Figure 3 shows the SEM images (at 800 X) of adsorbent surface, before and after adsorption. Before adsorption (Figure 1A), the surface is irregular and uneven, with trichomes specific to raspberry leaves. These specific formations have been (identified) emphasized in other studies that have analysed the SEM images of raspberry leaves [11].

After adsorption (Figure 1B), the surface morphology is modified. The surface of the dye-loaded adsorbent presents compact structure. Homogeneity and smoothness of the surface is due to the retained dye molecules, indicating that adsorption had occurred at the material surface.

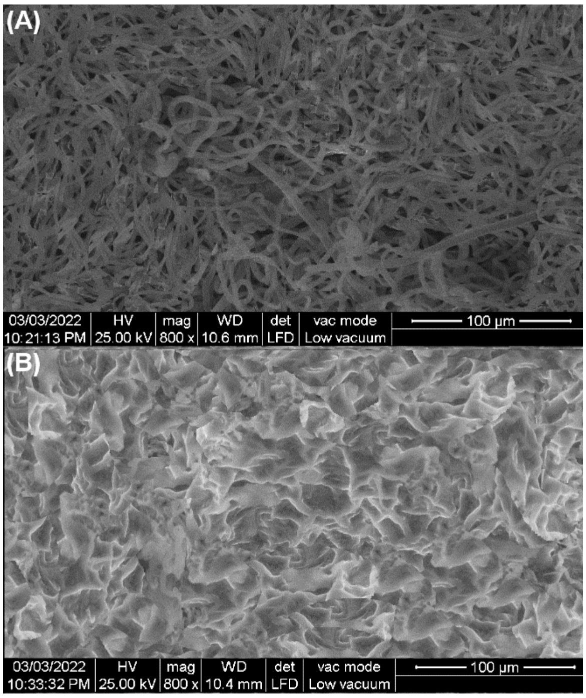

***Fig. 1.** SEM images of adsorbent surface before (A) and after (B) adsorption*

Colour analysis in the *CIEL*a*b** system was used to characterize the colour of the adsorbent, before and after desorption (Figure 2).

Before adsorption, the colour of the adsorbent material is described by point 1 and after adsorption

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by point 3. The crystal violet dye colour is described point 2. After adsorption, a change in the value of the colour parameters (*L**, *a**, *b**) is observed, which indicates the change of the adsorbent colour, point 3 being found in the colour quarter of crystal violet.

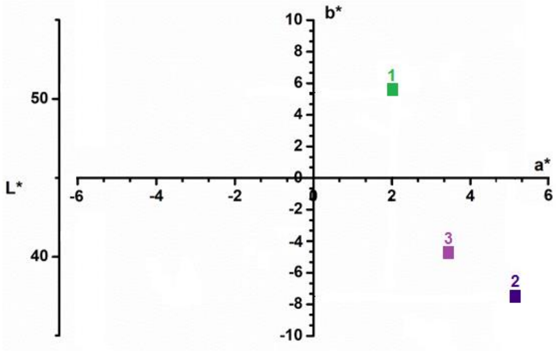

Fig. 2. CIEL*a*b* *colour parameters: 1- raspberry leaves powder; 2 - crystal violet dye; 3 - raspberry leaves powder after adsorption*

3.2. Influence of solution pH on adsorption capacity

The point of zero charge (pH_{PZC}) indicates when the adsorbent surface is positively or negatively charged depending on the pH. The pH_{PZC} of adsorbent materials was previously determined as 5.6 [13].

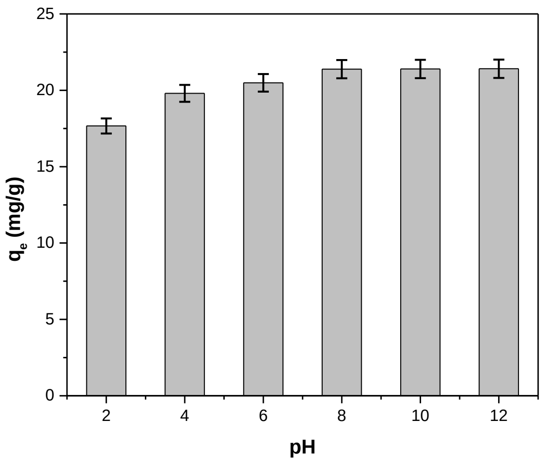

Fig. 3. *The influence of solution pH on adsorption capacity*

Figure 3 illustrate the influence of pH solution on the adsorption. The value of this parameter increases with the increasing of the pH. A similar observation was mentioned in other previous studies regarding the crystal violet dye adsorption of similar adsorbents obtained from vegetal wastes [4, 9, 17-19]. At lower pH values than pH_{PZC} (5.6) the adsorbent surface is positive charge and electrostatic repulsion occurs between cationic dye and raspberry leaves powder. At higher pH values than pH_{PZC} the adsorbent surface is negative and electrostatic attraction favours the process [9, 15, 19].

3.3. Influence of adsorbent dose on adsorption capacity

The adsorbent dose influence on adsorption capacity is shown in Figure 4. The increase of adsorbent dose has a negative effect on the adsorption capacity. A similar behavior was observed at crystal violet adsorption on *Ocotea puberula* bark powder [9], *Terminalia arjuna sawdust* [2], *Eragrostis plana Nees* [16], *Moringa oleifera* pod husk [17], coniferous pinus bark powder [20], rice bran [21], wheat bran [21] and corn stalk [22] and lilac tree leaves powder [23]. When the adsorbent dose increases, the available adsorption sites number increases, but many remain unsaturated. Agglomeration and aggregation of adsorbent material particles may occur at high adsorbent dose. This phenomenon's led to a decrease in the adsorption capacity [2, 21-23].

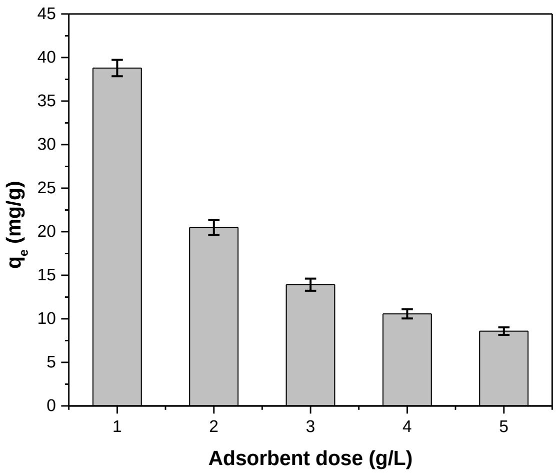

Fig. 4. *The influence of adsorbent dose on adsorption capacity*

3.4. Influence of initial dye concentration on adsorption capacity

The adsorption capacity is significantly influenced by the increase of the initial dye concentration. The positive effect is explained by the fact that the increase of the initial concentration of the dye favours the number of collisions between the dye and adsorbent molecules. At the same time, it increases the driving force required to overcome the mass transfer resistance of the dye from solution on the adsorbent surface [2, 4, 16, 17, 23].

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The same variation of the adsorption capacity with the initial dye concentration was reported to the crystal violet adsorption on *Terminalia arjuna* sawdust [2], cedar cone [4], *Ocotea puberula* bark [9], *Moringa oleifera* pod husk [17], *Punica granatum* shell [19] and corn stalk [22], lilac tree leaves powder [23], jackfruit leaf powder [24] and pineapple leaf powder [25].

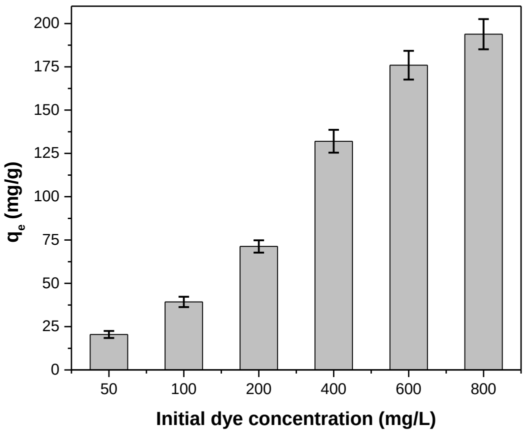

Fig. 5. *The influence of initial dye concentration on adsorption capacity*

The changes of the surface morphology and the adsorbent material colour, highlighted by the SEM and colour analyses, as well as the experimentally obtained values for the adsorption capacity demonstrate the affinity of raspberry powder for the violet crystal dye retention.

3.5. Adsorption isotherms

In order to study the equilibrium adsorption four isotherm were tested to fit the experimental data: Langmuir, Freundlich, Temkin and Sips. The isotherms curves for crystal violet dye adsorption are presented in Figures 6-9. The adsorption isotherms constants are shown in Table 1.

In order to establish the most suitable model that characterizes the adsorption process, the values obtained for determination coefficient (R^2), chi-square (χ^2) and average relative error (ARE) were taken into account.

$$R^2 = 1 - \frac{\sum_{i=1}^{n}\left(y_{i,exp} - y_{i,mod}\right)^2}{\sum_{i=1}^{n}\left(y_{i,exp} - \overline{y_{i,exp}}\right)^2} \quad (6)$$

$$\chi^2 = \sum_{i=1}^{n}\frac{\left(y_{i,exp} - y_{i,mod}\right)^2}{y_{i,mod}} \quad (7)$$

$$ARE = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{y_{i,exp} - y_{i,mod}}{y_{i,mod}}\right| \quad (8)$$

where: $y_{i,exp}$ represents the experimental value; $y_{i,mod}$ represents the modeled value; $\overline{y_{i,exp}}$ represents the mean values and n is the total amount of information [14].

Analysing the obtained data, it can be concluded that the Sips isotherm best described the crystal violet adsorption process on raspberry leaves powder (the higher value of R^2 and the lowest values for χ^2 and ARE).

The value of the maximum adsorption capacity obtained for the adsorbent material is higher compared to that of other similar adsorbents used for the retention of crystal violet.

Table 2 presents comparatively the maximum adsorption capacities values for several similar adsorbents.

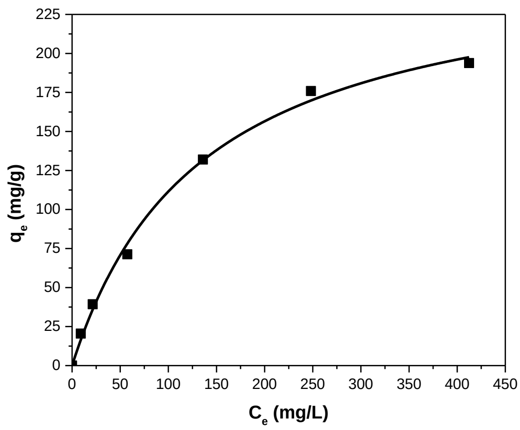

Fig. 6. *Langmuir isotherm for crystal violet adsorption on raspberry leaves powder*

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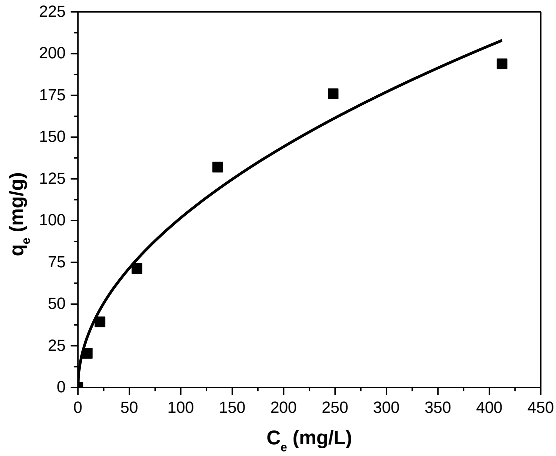

Fig. 7. *Freundlich isotherm for crystal violet adsorption on raspberry leaves powder*

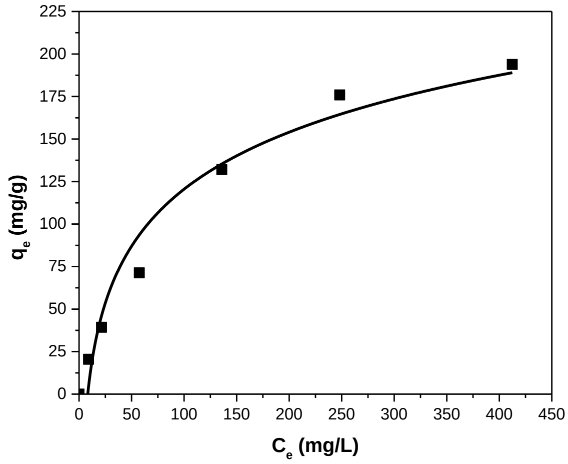

Fig. 8. *Temkin isotherm for crystal violet adsorption on raspberry leaves powder*

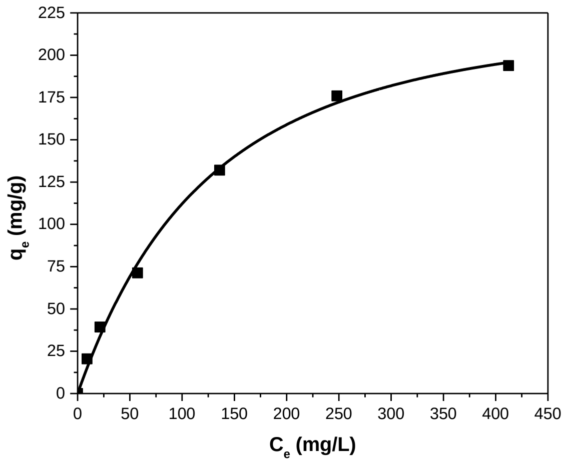

Fig. 9. *Sips isotherm for crystal violet adsorption on raspberry leaves powder*

Table 1. *The adsorption isotherms constants*

Isotherm model	Parameters	Value
Langmuir	K_L (L/mg)	0.007 ± 0.001
	q_{max} (mg/g)	262.4 ± 6.38
	R^2	0.995
	χ^2	2.22
	ARE (%)	6.97
Freundlich	K_f (mg/g)	9.92 ± 0.83
	1/n	0.50 ± 0.05
	R^2	0.978
	χ^2	8.54
	ARE (%)	11.79
Temkin	K_T (L/mg)	0.123 ± 0.042
	b (kJ/g)	50.55 ± 4.69
	R^2	0.972
	χ^2	70.69
	ARE (%)	62.75
Sips	Q_{sat} (mg/g)	264.5 ± 8.25
	K_S (L/mg)	0.007 ± 0.001
	n	0.99 ± 0.09
	R^2	0.997
	χ^2	2.07
	ARE (%)	6.65

Table 2. *Maximum adsorption capacities values of similar adsorbent materials used for the crystal violet dye removal from aqueous solutions*

Adsorbent material	**Maximum adsorption capacity (mg/g)**	**Reference**
water hyacinth root powder	322.58	[26]
raspberry leaves powder	**264.5**	**This study**
grapefruit peel	254.16	[28]
common lilac tree leaves powder	196.75	[23]
Moringa oleifera pod husk	156.25	[17]
wood apple shell	129.87	[18]
wheat bran	69.15	[21]
coir pith	65.53	[15]
Punica granatum shell	50.21	[19]
jackfruit leaf powder	43.39	[24]
rice bran	41.68	[21]
pinus bark powder	32.78	[20]
cedar cones	13.64	[4]
almond shells	12.20	[8]
corn stalk	9.64	[22]
pineapple crown leaves	6.49	[29]

The possibility of regeneration of the exhausted adsorbent was achieved using three desorption reagents: HCl (0.1 N), NaOH (0.1 N) and distilled water. The efficiency of the desorption process was less than 30% for all desorption agents tested. Based on these results and taking into account the fact that the raspberry leaves are a cheap material, easily accessible and available in large quantities, it can be concluded that regeneration is not rentable.

Based on its combustion properties the adsorbent resulting from adsorption can be incinerated in specialized incinerators. Another option is to be used as a porogenous agent for obtaining cellular glass and porous ceramic materials, due to the resulted gases in the thermal synthesis process of these products.

4. Conclusions

The adsorption capacity of the adsorbent material obtained from raspberry leaves is influenced by pH, adsorbent dose and initial dye concentration.

Sips isotherm best described the crystal violet adsorption. The obtained maximum adsorption capacity, 264.5 (mg/g) was higher compared to other similar adsorbents obtained from vegetal wastes.

The results of this study indicate that the raspberry leaves powder is very suitable for crystal violet adsorption from aqueous solutions.

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