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Valuation of Pomegranate Peel for Cationic Dye Removal

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ABSTRACT
In recent decades, the global production of pomegranate has increased considerably, leading to a remarkable increase in the amount of pomegranate peel generated. Hence, the need for its valuation. In this respect, the present work aims to attempt the potentiality of pomegranate peel as a low-cost adsorbent for methylene blue (MB) removal. The batch experiments were performed to determine the adsorption capacity of the biomass. The system variables studied include Adsorption time and initial dye concentration. It was shown that the MB adsorption onto pomegranate peel is drastically dependent on adsorption time and initial dye concentration. The rate adsorption of MB was rapid, attained equilibrium at about 60 min, a time in which the percentage removal exceeds 75%, and this at the initial dye concentration of 100 mg.L^{-1}. The results also show that pomegranate peel has a relatively higher adsorption capacity (67,78 mg.g^{-1}) than other biomass. That leads to contemplate the possibility that it can serve as a low-cost and eco-friendly adsorbent for the removal of other cationic dyes.
Keywords – Adsorption capacity, cationic dye, pomegranate peel, valuation, dye removal

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I. INTRODUCTION

Pomegranate is one of the trendy fruits, whether for its pleasant tangy and refreshing taste or its excellent nutritional and therapeutic properties. During the last decade, the pomegranate fruit and its extract have been shown to have preventive and mitigating activities against many disorders and chronic diseases. It is about cardiovascular diseases [1,2], type 2 diabetes [3], atherosclerosis, and some cancers [4,5].

The undeniable benefits and virtues of this harmonious large apple, making it a coveted fruit, thus encouraging their consumption. Given the strong demand for the fruit and its derivatives (juice, syrup, jam, etc.), the global production of pomegranate continues to increase to meet consumer needs. That results in a remarkable increase in the amount of pomegranate peel worldwide. It should be noted that the peel accounts for about 50% of the fruit mass [6], thus estimating its global production to be close to 1,9 million tonnes in 2017 [7]. Pomegranate peel is certainly quite famous for a set of uses given its particular composition. Nevertheless, a significant amount of this biomass finds its end as waste, without any economic value, given the importance of the volume generated. Hence, the need to resort to other valuation routes to exploit this orebody.

In this respect, we attempted to evaluate the potential use of pomegranate peel as a green adsorbent for dye removal. Furthermore, the presence of dyes on the surface water has a deleterious effect on aquatic life [8]. Even in small amounts, they are highly visible in water [9] and consequently decrease its transparency. That's leading to the inhibition of sunlight penetration necessary for the photosynthetic activity [10,11]. To remedy this situation, the removal of dyes from industry effluents is then a top priority.

In the present study, methylene blue dye was chosen to evaluate the performance of pomegranate peel concerning the issue of colored effluents. This dye is frequently used in various industries. Nevertheless, the risks for which it is responsible, once evacuated into the receiving environment, have drawn our attention.

II. MATERIALS AND METHODS

II.1. Adsorbate

The methylene blue (MB), with properties given in Table1, was purchased from Loba Chemie and used without any prior purification. The colored solutions for adsorption experiments were prepared by diluting 1g/L of the MB stock solution. This one was prepared by dissolving an appropriate amount of MB powder in distilled water.

Table 1. Properties of methylene blue

Characteristic	**Identification**
Synonym	Basic Blue 9
Chemical formula	$C_{16}H_{18}ClN_3S_3$
C. I. Number	52015
Molecular weight	319,859 g/mol
pH	5,95
λmax	660-665 nm

II.2. Preparation of pomegranate peel

Once separated from the fruit, pomegranate peel was rinsed thoroughly with distilled water and placed under direct sunlight for about twenty days until they become hard and give up all the moisture. Then these fragments were crushed. Afterward, to remove hydrolyzable tannins and any other impurities, the obtained powder was washed several times with distilled water until the supernatant was free of color. The decanted powder was dried at 60 °C for 48 h, then stored in a desiccator until use.

II.3. Adsorption experiments

Batch adsorption experiments were conducted for MB removal from aqueous solutions. They were carried out in copped conical flasks by introducing 0,1 g of pomegranate peel into 50 mL of the MB solution with an initial concentration C_0, without adjustment of the initial pH. These suspensions were maintained under magnetic stirring at an agitation speed of 300 rpm (Fig.1). After reaching equilibrium, the suspensions were centrifuged at 3800 rpm for 5 min. Then the MB concentrations in the supernatant solutions were analyzed using a double beam UV-Vis spectrophotometer at 665 nm.

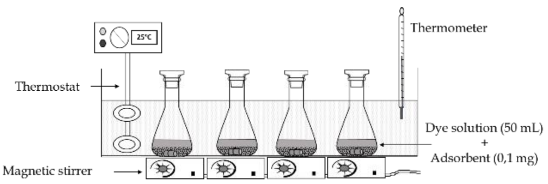

Figure 1. Adopted operating procedure for MB adsorption

All experiments were conducted at least twice times and the values were expressed on average. The adsorption rate (%R) and the adsorption capacity (q_e) were calculated by the following equations, respectively:

$$\%R = \frac{(C_0 - C_e)}{C_0} \cdot 100 \qquad (1)$$

$$q_e = \frac{(C_0 - C_e)}{m} \cdot V \qquad (2)$$

where C_0 and C_e are initial and equilibrium MB concentrations (mg/L), respectively. V is the volume of dye solution (L), and m is the mass of adsorbent (g).

III. RESULTS AND DISCUSSION

III.1. Adsorption time effect

The effect of reaction time on the adsorption capacity of MB onto pomegranate peel is shown in Fig.2. In the first 10 min, the adsorption rate increased rapidly and reached more than 60%. However, when the reaction time exceeded 10 min, the adsorption rate of MB increased slowly up to reach its equilibrium at about 60 min. Indeed, at this reaction time, the adsorption rate of MB is in the order of 75%. This observation can be attributed to the large number of active sites at the first stage, but over time they were progressively occupied, which leads to no more difference in the adsorption rate. A similar trend was also observed in previous work [12–14].

Furthermore, to investigate the effect of initial dye concentration, the adsorption time was set to 120 min, which is more than sufficient time to reach equilibrium.

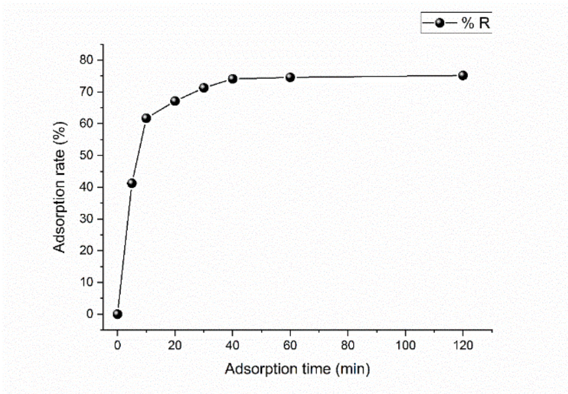

Figure 2. Time effect on the adsorption rate

III.2. Initial dye concentration effect

The effect of initial dye concentration on the MB adsorption was investigated over a concentration range of 100 - 500 $mg.L^{-1}$; while keeping every operating parameter constant. Fig.3 outlines that the adsorption rate of MB decreased significantly when the initial MB concentration increased. This observation can be explained by the availability of unoccupied binding sites on pomegranate peel at low initial dye concentrations. While at higher concentrations, the binding sites are almost completely covered, reducing the percentage of dye removal from aqueous solution.

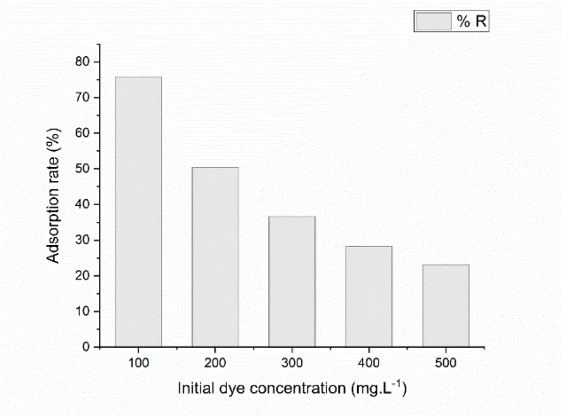

Figure 3. Initial dye concentration effect on the adsorption rate

In contrast to the adsorption rate, Fig. 4 shows that the adsorption capacity increased significantly when the initial MB concentration increased up to 400 mg.L^{-1}. That can be related to the enhance of driving force due to the concentration gradient [15]. Moreover, the maximum adsorption capacity was 67,78 mg.g^{-1}. The same findings were also observed by other researchers [16].

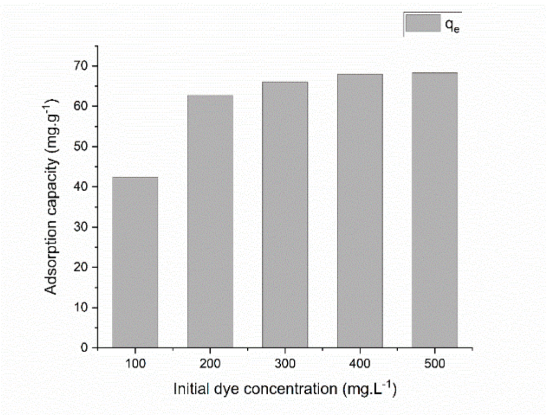

Figure 4. Initial dye concentration effect on the adsorption capacity

III.3. Adsorption capacity comparison

To further evaluate the performance of pomegranate peel for MB removal, it seemed judicious to compare its adsorption capacity with that of other biomass cited in the literature. Table 2 shows that pomegranate peel has a relatively greater adsorption capacity than others. That leads to contemplate the possibility that it can serve as a low-cost and eco-friendly adsorbent for the removal of other cationic dyes.

Table 2. Comparison of adsorption capacities of various biomass towards MB

Biomass	q_e (mg.g^{-1})	Reference
Pomegranate peel	67,78	This work
Orange albedo	77,79	[17]
Soursop residues	55,40	[18]
Sugarcane bagasse	17,43	[18]
Cortaderia selloana flower spikes	34,48	[19]
Wheat straw	60,66	[20]
Rice husk	40,59	[21]
Peanut hull	68,03	[22]
Raw date pits	80,29	[23]
Banana peel	20,80	[24]
Orange peel	18,60	[24]

IV. CONCLUSION

The present study reveals that pomegranate peel is an efficient and effective adsorbent for MB removal from aqueous solutions. The adsorption behavior of this cationic dye onto pomegranate peel was found to be drastically dependent on adsorption time and initial dye concentration. The rate adsorption of MB was rapid, attained equilibrium at about 60 min, a time in which the percentage removal exceeds 75%, and this at the initial MB concentration 100 mg.L^{-1}. The results gained from this study also show that pomegranate peel has a relatively higher adsorption capacity (67,78 mg.g^{-1}) than other biomass cited in the literature, highlighting the potentiality of this substrate for MB retention. Thus, this route of pomegranate peel valuation seems to be a win-win strategy that challenges the problem of dyes from industry effluents.

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