Aloe Vera waste for Methylene Blue (MB), Rhodamine B (RB) and Methyl Orange (MO) adsorption.

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Abstract Aloe Vera (*Aloe barbadensis miller*) waste obtained from a local cosmetic production factory was used as bio-adsorbent for the removal of three different dyes: Methylene Blue (MB), Rhodamine B (RB) and Methyl Orange (MO). The material was preliminary washed with water at room temperature. Batch tests at 25°C were performed and the experimental data were fitted using the pseudo-second order kinetic model. It was found out that the rate of adsorption for the tested dyes follows the order MO>MB>RB. Results show that the Aloe Vera waste can be successfully used to remove cationic dyes in aqueous solution. More precisely, 94% removal of MB, 71% removal of RB and a 13% removal of MO was observed in separate tests in which the starting concentration of the correspondent dye was set to 210 mg/L and the bio-adsorbent dosage to 20g/L.

Keywords: Adsorption; Aloe Vera; Data fitting; wastewater treatment.

1. Introduction

The removal of pollutants from wastewater is one of the most significant environmental challenge of the century. Lack of available water sources and tightening of regulatory standards of permissible component level make wastewater treatment essential and mandatory. Pollutants are characterized by a very wide range of toxicological profiles and physio-chemical properties. Dyes can perturb the biological activities of algae and plants by hindering light penetration in water. Moreover, they can develop allergies, dermatitis, and even cancers, through contact with the gastrointestinal tract, skin, and lungs (Sardar et al. 2021). Most of the wastewater treatment technologies have high operational and maintenance costs, i.e. replacement costs, generation of toxic sludge and difficulty of its disposal, complexity of the process involved (Schwarzenbach et al. 2010). Adsorption is instead a valid alternative because of ease of operation, and simplicity of design. Although activated carbons are worldwide recognized as the most performant adsorbents (Sulyman et al. 2017), their high activation cost led to search for new low-cost environmental friendly adsorbents. In particular, agro-industrial wastes seems to be a promising alternative. Aloe Vera (*Aloe Barbadensis Miller*) is a perennial, drought-resistant succulent herb, called the healing plant or the silent healer because of its wound and burn healing properties. The healthcare and cosmetics sectors are currently the two biggest drivers of Aloe Vera consumption. Thailand is the bigger producer (one-third of global production), followed by Mexico, Dominican Republic, United States and Costa Rica. The global Aloe Vera market size was US$602 Million in 2019 (IMARC Group), thus a large number of wastes are available to be recycled before disposal. Some studies used Aloe Vera wastes for adsorption of dyes from wastewater in form of non-treated materials, air-dried bio-sorbent, thermally dried biomass, carbonized and functionalized materials, chemically treated dried powder (Giannakoudakis et al. 2018). Untreated Aloe Vera waste was investigated to remove Methylene Blue (MB) from aqueous solutions under batch experiments (Hanafiah et al. 2018): MB adsorption was favored at pH> 3 and room temperature; data were fitted by Langmuir isotherm and maximum adsorbent capacity was 365 mg/g. Aloe Vera leaves were also used in the form of air-dried and thermally treated at 300-500°C (El-Azazy et al. 2019) to remove Titan yellow: results showed that air-dried had a better performance than thermally treated Aloe Vera, reaching maximum adsorption capacity of 52 mg/g. Aloe Vera waste was also investigated for the removal of Methylene Blue after activation at 1000°C (Abuthahir et al. 2017): removal percentage was 90% at 30°C by using an adsorbent dosage of 0.5 g/L and MB concentration of 50 mg/L. Aloe Vera leaves were sulfuric acid modified activated carbon in (Khaniabadi et al. 2016) for the removal of aniline and methyl orange, resulting in 185.18 and 196.07 mg/g maximum adsorption respectively. The present work investigated the potential of air-dried Aloe Vera as bio-adsorbent of Methylene Blue (MB), Methyl Orange (MO) and Rhodamine B (RB) as target dyes. Kinetics behaviors were fitted by the pseudo-second order model.

2. Materials and Methods

2.1. Bio-adsorbent preparation

The outer layer of Aloe Vera (*Aloe Barbadensis Miller*) leaf was obtained from residues of a cosmetic industry located in Lazio region, Italy. The solid was washed three times in distilled water at room temperature with a concentration of 50 mg/L for 2 h, then dried at 60 °C for 24 h. The bio-adsorbent was then grinded in order to obtain a size less than 5 mm.

2.2. Chemicals

Methylene blue (C16H18CIN3S; MB), Rhodamine B (C28H31ClN2O3; RB) and Methyl Orange (C14H14N3NaO3S; MO) were purchased from Sigma Aldrich (United States). All chemicals were of analytical reagent grade and used without any further purification. The solutions used in the experimental tests were prepared by providing a dilution in ultra-pure water.

2.3. Batch tests

Batch tests were conducted at 25 °C, neutral pH and a solid to liquid ratio of 20 g/L. Each dye was tested alone in every experiment. Kinetic tests were performed on 15 mL solution of MB, RB, and MO at an initial concentration of 9 mg/L, 8 mg/L and 14 mg/l, respectively. Equilibrium tests were performed at an initial concentration of 210 mg/L for all the dyes. The equilibrium test lasted 2 h. The concentration of MB, RB and MO was measured by spectrophotometric analysis using a PG Instruments (United States) T80+ UV/Vis spectrophotometer (with glass cells of 1 cm path length) at λ = 664 nm, λ = 554 nm and λ = 464 nm respectively. The percentage of the dye i removed at equilibrium (R_i%) was calculated with the following equation:

$$R_i\% = \frac{C_0 - C(t = 2h)}{C_0} \quad (1)$$

where C_0 (mg/L) is the concentration of MB at the beginning of the test and C(t=2h) (mg/L) is the concentration of MB calculated after 2 h.

3. Results and Discussion

The kinetics bath tests were performed to detect significant differences in the adsorption rate between the three dyes under analysis. In Figure 1 is reported the ratio between the concentration measured at a certain time respect to the initial concentration of the dye versus time. In order to quantify the adsorption rate, the data were fitted with the second order kinetic model which is expressed as follows:

$$\frac{t}{q(t)} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \quad (2)$$

$$\frac{C(t)}{C_0} = 1 - q(t)\frac{C_s}{C_0} \quad (3)$$

where q(t) (mg/g) is the amount of dye adsorbed respect to the grams of bio-adsorbent used, q_e (mg/g) is the amount of dye adsorbed respect to the grams of bio-adsorbent used at equilibrium, C_s (g/L) is the solid concentration and k (mg/g s) is the pseudo second order kinetic constant.

A non-linear regression was performed to fit the experimental data with Eq. (2) and (3) using as objective function the minimization of the mean square error

$$\emptyset = min\left[\frac{1}{N}\sum_{i=1}^{N}\varepsilon_i^2\right] \quad (4)$$

where N is the number of experimental points and ε_i is the error calculated by the difference of the experimental data and the values predicted by the model.

Figure 1 shows that the pseudo second order perfectly fitted the experimental data and the values of k and q_e resulting from fitting are reported in Table 1

Table 1. Values of k and q_e derived from fitting.

	k ($mg\ g^{-1}\ min^{-1}$)	**q_e ($mg\ g^{-1}$)**
MB	0.17	0.38
RB	0.13	0.31
MO	0.78	0.10

In Table 1 it is possible to observe, that the rate of adsorption follows the order MO>MB>RB. According to the molecular weights of the three dyes (which influences the sizes of the dyes and therefore their adsorption rate) this order should have been MB>MO>RB. A possible explanation of such phenomena was provided by Ocholi et al. (O.J et al. 2016) which attributed the faster adsorption of MO to its linear and flexible molecular structure compared to the one of MB.

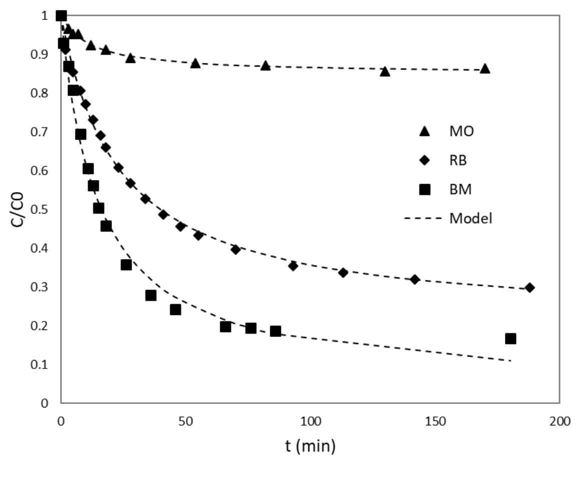

Figure 1. Kinetics batch tests performed with a solid dosage of 20 g/L at 25°C together with pseudo second order model fitting. Initial concentrations are 9 mg/L, 8 mg/L and 14 mg/l for MB, RB, and MO respectively.

On the other hand, the values of q_e obtained suggest that Aloe Vera affinity towards the adsorption of the analyzed dyes follows the order MB>RB>MO. Such observation is confirmed by Figure 2 in which are reported the removal percentage of dye after 2h batch test when the starting concentration was set to 210 mg/L for all the dyes. Since both MB and RB are cationic dyes while MO is an anionic dye, it was observed a higher adsorption affinity of Aloe respect to cationic dyes.

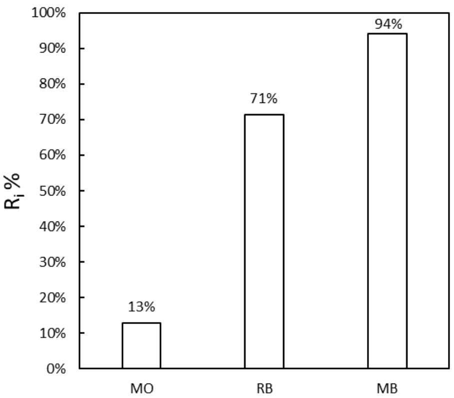

Figure 2. Dye removal percentage after 2h batch test at 25°C with a solid dosage of 20 g/L and an initial dye concentration of 210 mg/L (for all the different dyes).

4. Conclusions

This work investigated the potential of air-dried Aloe Vera to adsorb Methylene Blue (MB), Rhodamine B (RB) and Methyl Orange (MO). The proposed bio-adsorbent proved to be more efficient in the removal of the two cationic dyes MB and RB while it was less performant for the uptake of the anionic dye MO. However, by means of the pseudo-second order fitting, it was observed a higher adsorption rate for MO uptake. This result was attributed to the molecular flexibility of MO which can diffuse more rapidly respect to MB and RB towards the adsorption sites.

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