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The Use of Moringa Oleifera Seeds in the Retention of Basic Fuchsin Dye: Influence of Operational Parameters

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Moringa Oleifera Seeds (MOS) were used in their natural state, without preparation or chemical modification, to study the retention of Basic Fuchsin (BF) dye from aqueous solutions in a batch adsorber at room temperature. The characterization of the material was carried out by FTIR and SEM-EDX techniques. The pseudo-first order model describes well the adsorption kinetics. The adsorption isotherms of adsorbent/adsorbate systems are satisfactorily described by the Freundlich model which supposes a multilayer adsorption on heterogeneous surfaces. The experiments carried out have shown that MOS materials are suitable for discoloration of wastewater. They have a remarkable efficiency in the field of water treatment and can be envisaged for use as alternative adsorbent.

1. Introduction

Synthetic dyes represent a relatively large group of organic compounds found in virtually all spheres of our daily lives. Global production of synthetic organic dyes is estimated at 700,000 tons, of which 140,000 are released into effluents during the various stages of application and manufacturing (Zollinger, 1987), (Cooper, 1995).

These releases, composed of surfactants, biocidal compounds, dyes and trace metals, are toxic to most living organisms. The heterogeneity of their composition makes it difficult or almost impossible to obtain pollution thresholds lower than or equal to those imposed by environmental standards, after treatment by conventional techniques (Guivarch and Oturan 2004).

Treatment processes for industrial effluents containing dyes are of three types: biological processes (aerobic and anaerobic), chemical processes (oxidation, reduction, complexometric method) and physicochemical processes such as adsorption, reverse osmosis; filtration; coagulation-flocculation, etc.

Adsorption remains a relatively used and easy-to-implement technique that requires the use of synthetic materials as adsorbents which can be expensive and hazardous to health and the environment. The high cost of adsorbents leads researchers to find other less expensive substitutes such as natural adsorbents (Crini, 2006) that are mostly agricultural and industrial waste with intrinsic properties which give them a significant adsorption capacity (Özacar and Sengil, 2005), (Joseph, 2009).

Several by-products and agricultural or agri-food residues can be used as economic and eco-friendly adsorbents, such as fruit waste (olive pits; almond, apricot and peach shells, pomegranate and orange peel), (Boutemak et al., 2019), the agricultural waste: Xiuli et al. (2011) used lotus leaf for the removal of methylene blue, The industrial wastes: like carbon derived from tire rubber, treatment sludge, bagasse pith (which is a significant waste from the sugarcane industry), algae and seafood waste: such as green algae and chitin from the cell wall of some fungi. Liu et al. (2010) used this waste as a sorbent for the removal of methylene blue.

Biosorption offers several advantages such as low cost of adsorbents, high efficiency, minimization of chemical and/or biological sludge, and regeneration of the biosorbent. Natural sorbents can be considered as an excellent alternative for chemical remediation (Demirbas 2008), (Cleide et al., 2010).

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The aim of this work is the evaluation of a vegetable biomass, Moringa Oleifera Seeds (MOS) in their natural state, without preparation or chemical modification, as an alternative, low-cost effective adsorbent for the retention of a cationic dye: Basic Fuchsin (BF) from aqueous synthetic solutions in a batch adsorber at room temperature. Fuchsin inhibits the growth of algae and small crustaceans for minimum concentrations of $1\ \mathrm{mg.L^-}$ and $20\ \mathrm{mg.L^-}$ respectively (Meinck et al., 1977). Several types of natural sorbents (biomass) have been used for BF retention from aqueous solutions (Baara and Mecheri, 2020).

Moringa Oleifera is a plant native to the Agra and Oudh regions of northeast India, south of the Himalayan mountain range, but it is cultivated today in all tropical and subtropical regions of the world. The Moringa Oleifera plant can be found in very arid areas like the Sahara, but it prefers humid semi-tropical climates. Moringa Oleifera is the best known species of the Moringaceae family (Araújo et al., 2010).

The dried seeds of Moringa Oleifera contain active cationic polyelectrolytes (protein) which have proven their effectiveness in water treatment. They neutralize the colloids in muddy or dirty water since the majority of these colloids have a negative electrical charge. This protein can therefore be used as a non-toxic natural polypeptide for sedimenting mineral particles and organics in the purification of drinking water, for cleaning vegetable oil, or for sedimenting fibers in the juice and beer industries. MOS have been employed with particular effectiveness in both Egypt and Sudan for cleaning water from the Nile specifically for human consumption (Foidl et al., 2001). Yehe and Gbassi (2019) showed that MOS have an amorphous character suggesting that the aqueous mineral pollutants could more easily penetrate the surface and thus facilitate the phenomenon of sorption.

2. Materials and Methods

2.1 Preparation of the biosorbent

Biosorbent was prepared from Moringa Oleifera Seeds in their natural state and without modification or chemical preparation. It was obtained after manual shelling of the fruit of the plant then washing with distilled water and drying until the seeds hardened in the open air and also in an oven between 50 and 60℃ in order to prevent a possible alteration of the physicochemical properties of the biosorbent.

2.2 Preparation and dosage of Basic Fuchsin dye solutions

Dye stock solution of $1\mathrm{g.L^-}$ was prepared by dissolving an appropriate quantity of BF (dark green coloured powder ≥ 85%, purchased from Sigma-Aldrich PANREAC) in bidistilled water. BF standard solutions at different concentrations were prepared by successive dilutions to build a calibration curve used for the determination of final BF concentration after the sorption by the analysis of residual BF using a UV spectrophotometer (PharmaSpec Model UV 1700) at 547 nm. The initial pH was adjusted from 2 to 11 using dilute solutions of HCl (0.1M) and/or NaOH (0.1M). The chemical structure of BF ($C_{20}H_{20}ClN_3$) is shown in Figure 1.

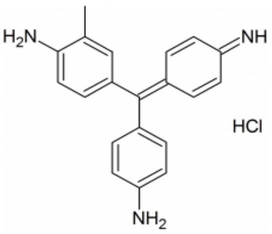

Figure 1: Structure of Basic Fuchsin Dye

The adsorbed quantities of BF (Q_t) at time t and at equilibrium (Q_e) per unit mass of material were calculated from equation 1 and 2. To estimate the BF retention efficiency $(E\ \%)$ on MOS the equation 3 was used.

$$Q_t = \frac{C_0 - C_t}{m}\ x\ V \qquad (1)$$

$$Q_e = \frac{C_0 - C_e}{m}\ x\ V \qquad (2)$$

$$E\ (\%) = \frac{C_0 - C_t}{C_0}\ x\ 100 \qquad (3)$$

Where : $\mathrm{C_0}\ (\mathrm{mg.L^{-1}})$, $\mathrm{C_t}\ (\mathrm{mg.L^{-1}})$, $\mathrm{C_e}\ (\mathrm{mg.L^{-1}})$ are respectively : the initial, the final concentration of BF (at time 0 and t) and at equilibrium in the aqueous solution, V is the aqueous solution volume (V=100 mL) and m (g) represents the sorbent amount.

2.3 Batch adsorption experiments of Basic Fuchsin on MOS- kinetic study

Adsorption experiments were carried out in batch mode at room temperature, using 250 mL erlenmeyer flasks closed-cap, containing an appropriate MOS quantity and a volume of 100 mL of BF solution was added, separately, at fixed initial concentration and constant pH. The assembly was placed under horizontal stirring on an oscillating table at room temperature. At the end of each stirring time, which was varied from 0 to 24 hours. The samples were filtered then analyzed directly by UV-Visible at 547 nm to determine the BF residual concentration in order to investigate the experimental parameters for dye removal, such as the contact time, the sorbent mass, the pH and the initial dye concentration.

3. Results and Discussion

3.1 Characterization of Moringa Oleifera Seeds (MOS) by FTIR

The IR spectrum (Figure 2) shows the existence of numerous functional groups within the biomaterial, indicating thus its complex nature. Two wide bands are identified, between 3400–3200 cm^{-1} which can be attributed to the hydrogen elongation vibrations of asymmetric O-H hydroxyls groups present in: proteins, fatty acids, cellulose, pectin, carbohydrates and lignin units present in MOS and/or adsorbed water. Due to the high protein content in these seeds, these two bands may contribute equally to the N-H stretching of the amide bond.

In addition, two high intensity bands at 2900 cm^{-1} and 2854.45 cm^{-1} were detected probably linked to the asymmetric C-H stretching vibrations of the aliphatic molecules.

In the region between 1760 and 1400 cm^{-1}, several bands are observed and can be attributed to the stretching of the C=O carbonyl bond (high intensity band at 1745.46 cm^{-1}). Due to the heterogeneous nature of MOS, the carbonyl group can be linked to different parts including the lipid part of fatty acids at 1745.46 cm^{-1} (a strong band) or the protein part of amides at 1656.74 cm^{-1}. A stretching of the bond between the C≡N group and/or a deformation of the N-H bond present in the seed proteins is observed at 1544.88 cm^{-1} which can confirm the protein structure in MSO. In addition, ester stretching vibrations accompanied by several bands around 1161.07; 1116.71; 1101.28 and 1058.85 cm^{-1} attributed to asymmetric and symmetric stretching vibrations of C-O-C.

Two bands observed at 1460.01 and 1421.44 cm^{-1} are attributed respectively to (CH_2) shear and (C-C) aromatic (conjugated to C=C). The bands observed at 1375.15; 1348.15 and 1236.29 cm-1 are attributed respectively to the absorption by C-H and C-O elongation in the acetyl groups of the methoxy groups of lignin and hemicelluloses. A low intensity band is located at 877.55 cm-1, can be attributed to the β-carbohydrate bonds between sugar units in hemicelluloses and cellulose (Araújo et al., 2010).

3.2 Characterization of MOS by SEM- Energy Dispersive X-ray (EDX) technique

SEM image of a MOS (Figure 2b) shows that the morphology of MOS shows a heterogeneous matrix which is relatively porous. This structure facilitates the sorption processes, due, especially, to the presence of the protein component of the seed. Thus, it can be concluded that MOS has an adequate morphological profile to retain the used dye. The EDX microanalysis is a technique of elemental analysis associated to electron microscopy. It reveals the presence of elements present in the specimens. Figure 2c shows clearly the complex nature of this biomaterial and the presence of the different elements constituting the MOS such as: Carbon, Oxygen, Nitrogen, Sulphur, etc., in different quantities.

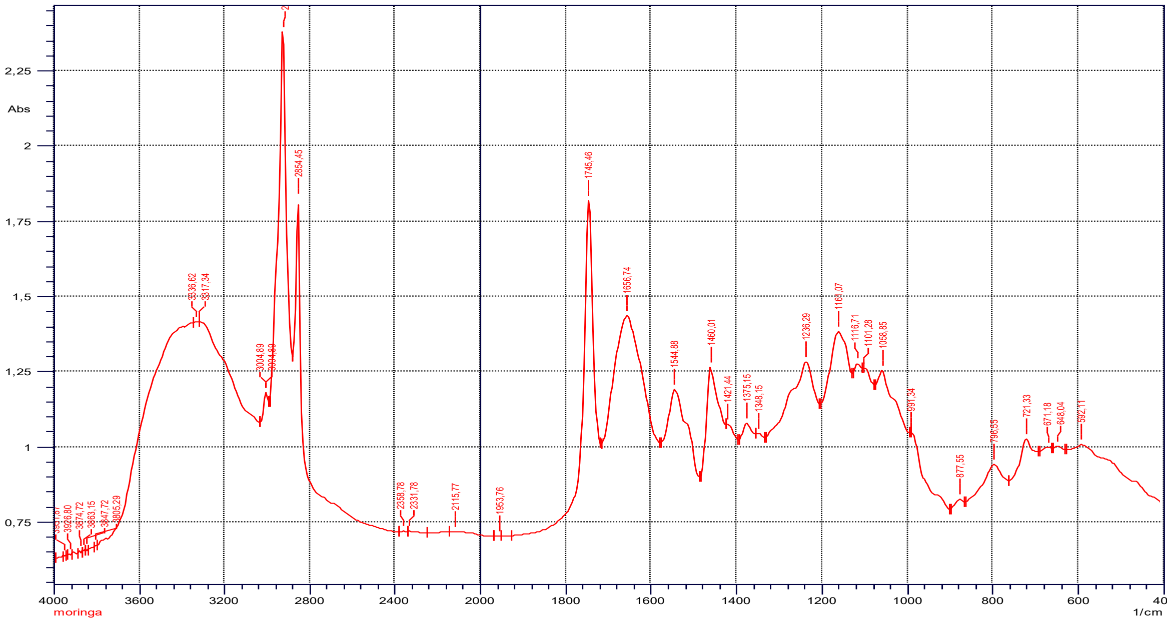

Figure 2: FTIR spectrum of MOS

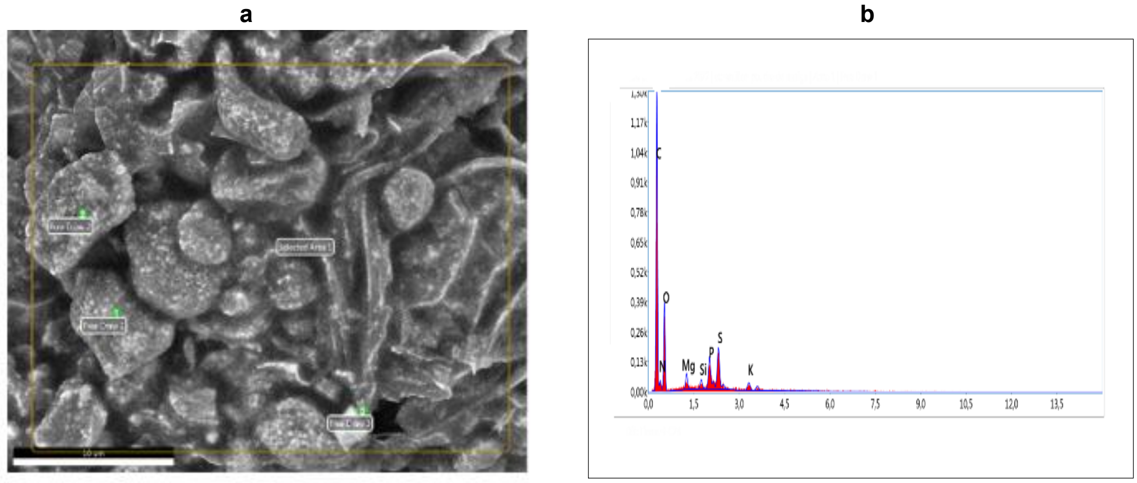

Figure 3:(a) SEM image of MOS, (b) SEM-EDX of MOS

3.3 Sorption of Basic Fuchsin onto MOS

3.2.1 Effect of contact time

Obtained results (Figure 4a) show that the sorption kinetics of BF at $10\mathrm{mg.L}^{-}$ on 1g of MOS increases with time until reaching a pseudo equilibrium after 3 hours. Yield stabilizes at 61.62%. 3 hours was then considered as sufficient for maximum retention.

3.2.2 Effect of biomaterial mass

Figure 4b shows that sorption yield of BF increases with MOS amount from 0.2 to 1.5 g. A pseudo-equilibrium state is reached at 1.2 g where the retention yield is about 60%. 1.2 g of MOS was chosen then for the rest of the work.

3.2.3 Effect of Basic Fuchsin solution pH

Results (Figure 4c) show that indeed, at pH values lower than MOS' pHpzc of 6.36 (Abbas and Boubekeur, 2020), the biosorbent is positively charged which implies interactions between the positively charged sites of the biomaterial and the cationic dye (pKa =2.1). On the other hand, at pH levels above 6.36, the biosorbent is negatively charged which generates electrostatic repulsions between the anions of the dye and MOS surface. The best retention efficiency of BF dye is 42.37%. Therefore, a pH of 5.6 (that of the prepared synthetic solution) is considered to be the optimal pH.

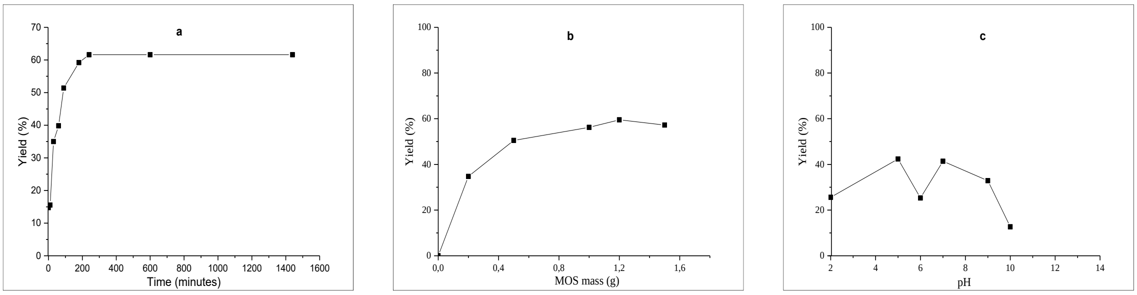

Figure 4: (a) Effect of contact time, (b) Effect of MOS mass, (c) Effect of pH

3.4 Biosorption kinetics

Application of two known order models, the pseudo-first-model and pseudo-second-model, to test experimental datat in order to investigate the BF sorption processes on MOS biomass reveals that pseudo first order model is best suited to describe the behavior of BF on MOS with correlation coefficient R^2=0.9956 and an equilibrium adsorbed quantity of $2.49\ \mathrm{mg.g^{-1}}$ (Table 1) .

Table 1: Kinetic model of BF sorption on MOS biomass

Pseudo-first-model			Second-first-model		
$\mathrm{Ln(Qe - Qt) = LnQe - K_1\,t}$			$\frac{\mathrm{t}}{\mathrm{Qt}} = \left(\frac{1}{\mathrm{Q_e^2\ K_2}}\right) + \left(\frac{1}{\mathrm{Q_e}}\right)$		
Qe	K_1	R^2	Qe	K_2	R^2
2.49	0.037	0.9956	0.553	0.00088	0.9837

3.5 Biosorption isotherms of Basic Fuchsin on MOS

Langmuir and Freundlich equations were employed to describe the equilibrium data. The performance of each form was judged through the correlation coefficients R^2. Obtained results show that data are well described by the Freundlich model (Table 2). The value of b, the (non-dimensional) parameter of Hall, in Langmuir model is equal to 6.32 > 1 indicates a defavorable isotherme of Langmuir. Moreover, the Freundlich constant K_F reflects the adsorption capacity of an adsorbate considered by the solid (Monarrez, 2004, Taoualit et al., 2021), more the value of K_F is high more the retained quantity is important (Ben Hamouda et al., 2017). In the case of this work, K_F =0.014 < 1, indicating a low affinity of MOS for BF according to the classification of Jamet (Jamet, 1988). The localized sites on the MOS surface receive BF in multilayers with possible interactions between the retained molecules. This biosorbent surface is heterogeneous, which means that all the exchange sites have the same affinity for BF.

Table 2: Langmuir and Freundlich sorption isotherms parameters of BF on MOS

Freundlich model			Langmuir model		
$\mathrm{Ln\ Q_e = Ln\ K_f + n\ Ln\ C}$			$\frac{\mathrm{t}}{\mathrm{Q_t}} = \frac{1}{\mathrm{Q_e}}\mathrm{t} + \frac{1}{\mathrm{K_2 Q_e^2}}$		
$\mathrm{K_f}$	n	R^2	$\mathrm{Q_m(mg.g^{-1})}$	$\mathrm{b} = \frac{1}{1 + \mathrm{K_L} C_0}$	R^2
0.014	1.06	0.806	0.01	6.32	0.0002

4. Conclusions

This study focused on the use of a biomass, the Moringa Oleifera Seeds (MOS), as an effective low cost material for the removal of Basic Fuchsin (BF) dye from aqueous solutions in a batch reactor at room temperature. The characterization of MOS by FTIR and SEM-EDX techniques show its complex nature and the high heterogeneous matrix which is relatively porous.

Results of Influence study of certain parameters on the yield and the retention capacity of the dye on MOS show that the retention of BF on MOS is indeed influenced by the variation of pH. Equilibrium is reached during 3 hours at pH of 5 on 1.2 g of the biomaterial. About 42% of BF was reached under these conditions.

The pseudo-first order model describes well the sorption kinetics. Sorption isotherms of biosorbent/sorbate systems are satisfactorily described by Freundlich model which supposes a multilayer retention on heterogeneous surfaces. The experiments carried out have shown that MOS materials are suitable for discoloration of wastewater. They have a remarkable efficiency in the field of water treatment and can be envisaged for use as alternative adsorbent since the procedure is simple, economically accessible and contributes to minimizing environmental impacts.

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