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Selective removal of dual dyes from aqueous solutions using Metal Organic Framework (MIL-53(Al))

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Abstract

The adsorption process of the cationic dye Malachite Green (MG) and the anionic dye Methyl Orange (MO) onto a MOF, namely, MIL-53(Al) was studied under several experimental parameters. Batch experiments were performed to investigate the feasibility of this MOF as possible adsorbent for the removal of MG and MO from both single and binary-dye aqueous solutions. Experimental results revealed that MIL-53(Al) can quickly bind to both types of dyes with high removal efficiency of more than 95%. The effects of different parameters such as adsorbent dosage, initial concentration of dye solution, pH of the solution, and temperature on the adsorption process were examined. Adsorption kinetic data were then fitted using pseudo first-order, pseudo second-order, and elovich models, showing that pseudo second-order model had the best fit for both dyes among the other models in both single and binary-dye systems with R^2>0.996. Moreover, adsorption isotherm models of Langmuir and Freundlich were studied and the isotherm data was found to be in good agreement with the Freundlich isotherm for both dyes. Thermodynamics studies of change in Gibbs free energy, enthalpy, and entropy were carried out and showed that the adsorption of both dyes was endothermic and spontaneous. The selectivity test for an equimolar binary-dye solution containing both MG and MO suggested the higher affinity of MIL-53(Al) towards MO over MG, as it reached a value of 13.58 at the optimum conditions. Finally, excellent reusability of MIL-53(Al) was shown by utilizing it for 4 cycles of adsorption-desorption with almost no reduction in the adsorption capacity, bringing about additional examination of its applicability.

Keywords:
Wastewater treatment
Adsorption
Metal-organic frameworks (MOFs)
Malachite green
Methyl orange
MIL-53(Al)

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Introduction

Environmental pollution has reached a disturbing level that is increasingly threatening the environment. This is due to the fast urbanization and the constantly growing world population not to mention the fast industrialization which generates wide quantities of dangerous wastes and lethal gases besides the required products. Critical water pollution happens when industrial outflow produces risky wastewaters that are emitted into the environment without being treated. It has been discovered that different pollutants like dyes, pharmaceutical and personal care products (PPCPs), herbicides/pesticides, spilled oil, persistent organic pollutants (POPs), and heavy metal ions are present in the various water resources [1].

Organic dyes released from many industries can be a threat to the environment and living creatures. Textile, leather, and paper industries are some of the important industries that require the utilization of synthetic dyes due to their color giving characteristics. It is reported that 700 000 tonnes of different coloring from around 100 000 attainable dyes are produced annually [2]. The majority of dyes are discharged without additional care into the aquatic environment as soon as their objective is fulfilled. The textile industry is declared to use and produce the largest amount of dyestuff and dye wastewater at roughly 10 000 tonnes and 100 tonnes each year, respectively [1], [2]. The massive water demand and the high utilization of pigmentation in the processes of this industry produce great amounts of dye wastewater. Such processes include dyeing, bleaching, wet finishing, scouring…etc. As soon as the process is finished, the mixture remaining from the preparation of certain blends of pigmentation, chemicals and water is discarded into the environment. The failure of the dye mixture, that is the dye chemicals and molecules, to be fully attached on to a textile or cloth results in the existence of dye effluents remaining from the textile industry. Plenty of dangerous chemicals are present in the dye wastewater, which can jeopardize the humans and animals' lives since they are naturally toxic. Some of these chemicals include acetic acid, soap, softener, caustic soda…etc. [3].

The self-purification and the oxygen transfer techniques of water reservoirs will become disrupted when acidic dye effluents at high temperatures are discharged instantly following dyeing processes. The ecosystem will be threatened by these effluents which will pollute the water bodies making them unfit for utilization. Since they have a lower density of 0.8 kg/m^3than that of water, 1.0 kg/m^3, dye effluents will create a visual layer on top of the water surface causing an increase in water turbidity. This prevents the permeation of sunlight needed by water living beings for photosynthesis and respiration kind of processes ending their lifetime. Contact with dye effluents can result in skin irritation; that is eye burns or everlasting eye damage. Inhalation of the chemicals existing in the dyes that are disposed into water after evaporation can cause breathing difficulties. Ingestion of dyes can result in nausea and mouth burns. So, wastewater must be treated from dye effluents to cease their harmful effects on the living things [3].

Previously, disposal of dye wastewater into the environment was not given careful thought. Light was shed on this problem after health issues began to emerge in the past 30 years [4]. After that, in order to come up with solutions, information on dyes, their utilization, and their removal methods were researched. Plenty of pollutants exist in dye wastewater like dissolved salts (TDS and TSS), chemical oxygen demand (COD), biological oxygen demand (BOD), colors and hazardous chemicals [3]. Recently, many researches are being conducted to discover the perfect dye removal technique in order to retrieve and reuse the dye wastewater [5]. Regardless of the existence of a good deal of methods of dye removal from wastewater, all these techniques have ingrained limitations and their own features and drawbacks. The methods can be separated into three classes: biological, chemical and physical treatments [6]. Physical dye removal methods have a removal percentage ranging from 86.8 to 99% with the adsorption method ranking the highest [3]. Adsorption stands out as one of the favorite dye removal methods among the countless tried-and-tested techniques because of its excelling capability to remove nearly any kind of dyes [7], [8]. Purification of industrial wastewater or cleaning drinking water can also be achieved by this method. Traditional techniques have been proven ineffective in removing synthetic dyes from dye effluent since they are incapable of entirely removing the dye from wastewater. So, adsorption is considered one of the best possible dye removal techniques as higher treated water quality is generated compared to other techniques. Adsorption is a non-reactive, mass transfer process illustrated by the cumulation of a material at the interface between two phases (liquid-solid interface or gas-solid interface). Adsorbate is the material that piles up at the interface while adsorbent is the solid on which adsorption happens [9]. A wide variety of adsorbents have been used to remove different types of dyes form water and wastewater. Some of them include: activated carbon, zeolites and metal organic framework (MOFs).

Great attention has been drawn to MOFs in academia and industry due to their versatility and possible utilizations. Since MOFs have possible applications in several areas, the research and number of publications associated to MOFs has grown quickly [10] . There are various appealing features that make MOFs distinctive and unlike other traditional permeable solids. These contain (1) straightforward and convenient synthesis compared with zeolites [11]. (2) large surface areas and adjustable porosities [12]. (3) the existence of coordinatively unsaturated sites (CUSs) or open metal sites (OMSs) [13] and (4) the capability to incarnate certain operations / active species without changing the framework topology [14]. Aluminum (III)-based MOF (MIL-53(Al)) is among the most attractive MOFs because of its breathing effect and being stable both in acidic and neutral aqueous mixtures [15]. It has also been extensively studied for water treatment and hydrogen storage [16].

Materials and Methods

Materials

MIL-53(Al) was supplied by Sigma-Aldrich (USA) under trademark Basolite® A100 and was utilized without additional purification. Malachite Green was purchased from Sigma Aldrich (USA) as 10,000 mg/L stock solution. Methyl Orange was purchased form LabChem (USA) as 1,000 mg/L stock solution. Various concentrations of MG and MO solutions were prepared by subsequent dilution using distilled water. Hydrochloric acid (37%) and sodium hydroxide (98%) were utilized for pH alteration for the preparation of 1.0 M aqueous solutions of HCl and NaOH. Ethanol (70%) was used for the renderability of the MOF (MIL-53(Al)).

Characterization

Multiple methods were used for the characterization of MIL-53(Al) in order to study the effect of adsorption of MG and MO. The crystalline structure of the MOF was determined by X-ray powder diffraction (XRD). A Bruker advance device was used to collect XRD samples with Cu Kα radiation and a linear detector (Germany, AXS D8). The scanning range over which the measurements were carried out was of 5-60^o with a 0.03^o step size. Fourier transform infrared spectroscopy (FT-IR) were performed using FTIR spectrophotometer (PerkinElmer, USA) at 4000-400 cm^{-1} scanning wavelength range by utilizing KBr pellet pressing technique. Signal-averaging of 10 scans were taken at a 1.0 cm^{-1} resolution. The work done by Milonjić et al. was used to determine the point of zero charge, pH_{pzc}, of MIL-53(Al) [17]. The patterns of MIL-53 (Al) before and after the adsorption process of MG and MO dyes were reported.

Batch Adsorption Experiments

For the single-dye adsorption, the aqueous solutions were prepared by consecutive dilution of the stock solution of MG or MO with distilled water. While, for the binary-dye (MG-MO) adsorption, certain amounts of stock solutions of MG and MO were diluted all together with distilled water to prepare the aqueous mixtures. A UV-Vis Spectrophotometer (Thermo Scientific, Evolution 60s, USA) was used to measure the absorbance of the prepared solutions in order to identify the concentration of MO and MG by using their calibration curves. The calibration curve for each dye was attained by using a set of standard solutions at different concentrations (1-30 mg/L) and was found to be linear and consistent over the utilized concentration range. This was done by serial dilutions of the stock solution for both MG and MO, for which no artificial adjustment of the pH was made. The batch experiment was performed by adding certain amounts of MOF adsorbent to 50 mL beakers that contained 50 mL MG, MO or MG-MO solutions with various initial concentrations (7-13 mg/L) at a certain pH and temperature. To prevent possible water vaporization, these beakers were sealed and then a magnetic stir plate was used to mix the solutions and make sure they were homogeneous in consistency and temperature. The solutions were then kept for a certain amount of time (5 min to 3 hr) to guarantee complete adsorption and achieve equilibrium. Using a 5 mL syringe, the samples were taken then filtered by membrane filters (Nylon, 13 mm diameter, 0.45 μm pore size). Following that, the UV-Vis spectrophotometer was used to measure the residual concentrations of Malachite Green and Methyl Orange in the sample at maximum wavelengths of 617 and 464 nm, respectively in case of single-dye solutions. For binary-dye solutions, the maximum wavelength for MO shifted to 430 nm while stayed the same for MG (617 nm). Furthermore, every experiment was performed in replicate and the standard deviation values were recorded.

The amounts of adsorbed MG and MO per unit mass of the adsorbent at time t, (q_t (mg/g)) and at equilibrium, (q_e (mg/g)) were calculated by equations (1) & (2), respectively.

$$q_t = \frac{(C_o - C_t) \times V}{m} \tag{1}$$

$$q_e = \frac{(C_o - C_e) \times V}{m} \tag{2}$$

where C_o is the initial concentration of MG or MO solution (mg/L), C_t is the residual concentration of MG or MO solution at time t (mg/L), C_e is the residual concentration of MG or MO solution at equilibrium (mg/L), V is the total volume of the solution (L), and m is the mass of the MOF used (mg).

For binary-dye adsorption, equimolar MG/MO solutions were prepared with initial concentrations in the range of 7-13 mg.L^{-1} for each dye and added to 50 ml beakers, to which MIL-53(Al) was added in amounts of 10 – 50 mg. The selectivity (dimensionless) of MIL-53(Al) can be calculated according to equation (3) [18].

$$Selectivity = \frac{q_{e,1}/C_{e,1}}{q_{e,2}/C_{e,2}} \tag{3}$$

where $C_{e,1}$ and $C_{e,2}$are the solution concentrations of dye 1 and dye 2 at equilibrium ($mg.L^{-1}$), respectively. $q_{e,1}$ and $q_{e,2}$ are adsorption capacities of dye 1 and dye 2 at equilibrium ($mg.g^{-1}$), respectively.

Results and Discussion

Characterization

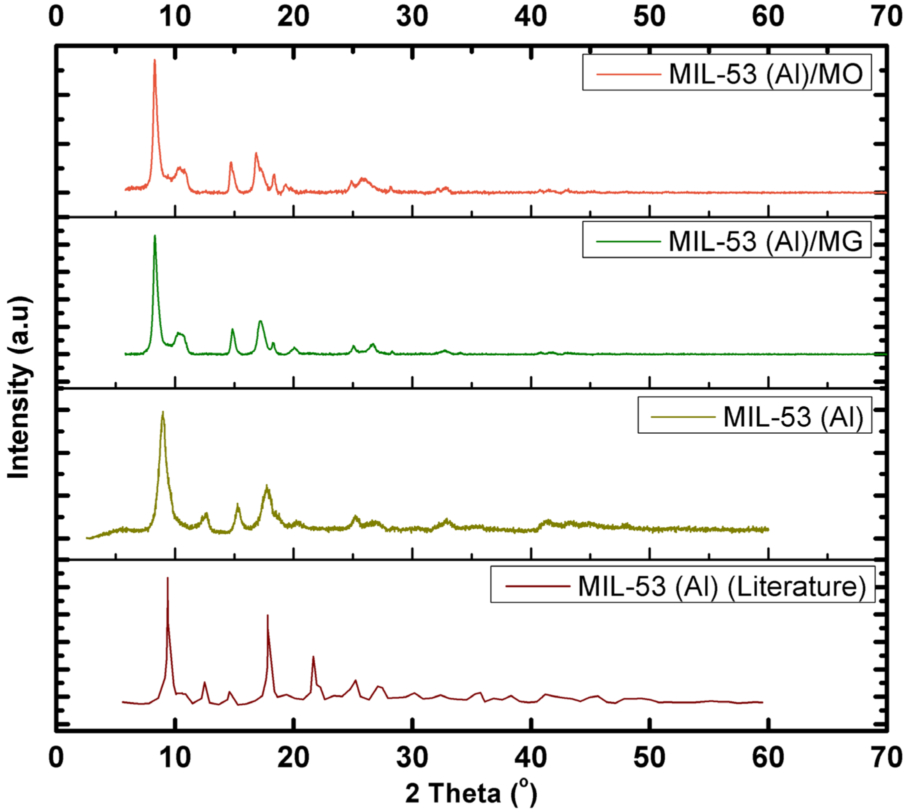

Fig. 1 XRD patterns of MIL-53(Al) before and after MO and MG adsorption. Pattern from literature reported by Li et al. [15].

The XRD patterns of MIL-53 (Al) before and after the adsorption process of MG and MO dyes are shown in Fig. 1. It can be seen that the commercial XRD patterns of the MOF's samples are consistent with the simulated ones reported in literature for the as-synthesized samples prepared in lab [15], [16], [19].

The XRD spectra of MIL-53(Al) present six characteristic peaks at 2θ of 8.98°, 12.72°, 15.26°, 17.78°, 25.46°, and 33°. These peaks are intense and precise, suggesting that MIL-53(Al) has a good crystallinity as well as a fine structure. It is observed that there is no major change in the diffraction patterns of MIL-53(Al) after adsorption of MG and MO dyes when compared to the one before the adsorption process. This implies the conservation of the crystalline structure of MIL-53(Al) after being exposed to MG and MO dyes for certain periods of time.

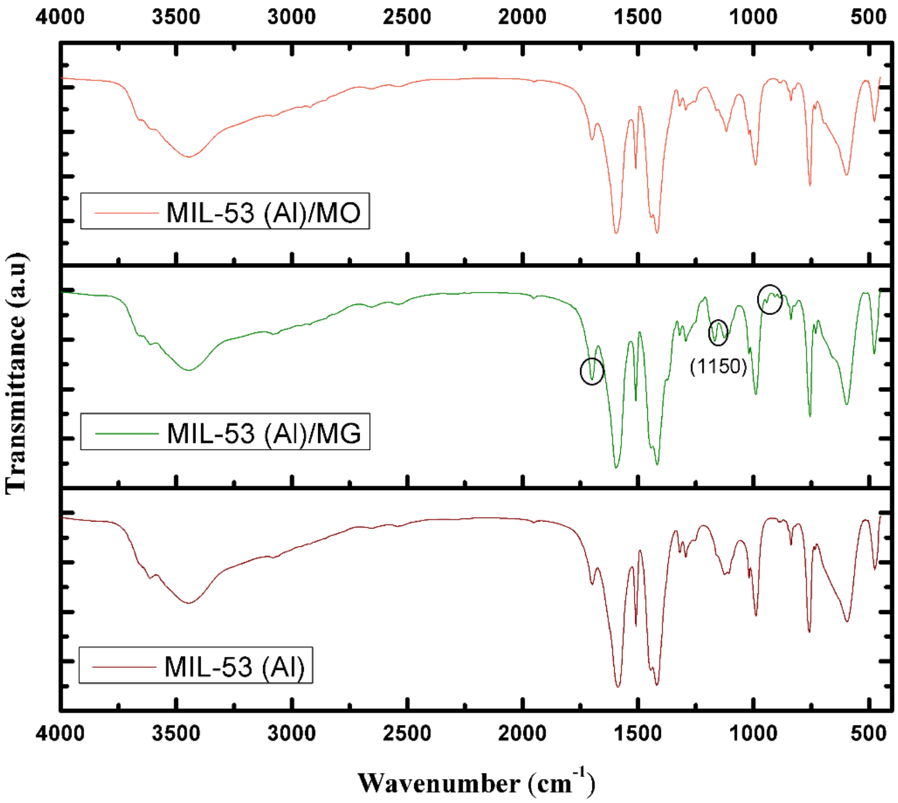

Fig. 2 FT-IR spectra of MIL-53(Al) before and after MO adsorption

FT-IR spectra of MIL-53(Al) before and after the adsorption process are demonstrated in Fig. 2. It can be seen that the obtained results are similar to those previously reported in the literature [20], [21]. The absorbance peak at 3495 cm^{-1} is assigned to -OH stretching vibration of adsorbed water on the surface [15]. Water molecules are present in MIL-53(Al) sample prior to adsorption due to the fact that this MOF absorbs some moisture from the air. However, after adsorption, the peak is still present due to the adsorption of water molecules from the prepared dye solution. The peak at 1690 cm^{-1} corresponds to -C=O stretching vibration [15]. The appearance of the peaks at 1596 and 1510 cm^{-1} is associated with the dissymmetry stretching vibration v_{asym} (CO_2^-) of –(O-C-O)- [15]. On the other hand, symmetry stretching vibration v_{asym} (CO_2^-) of –(O-C-O)- explains the peaks present at 1510 and 1416 cm^{-1}. The presence of peaks between 1260 to 965 cm^{-1} is because of the aromatic C-H in-plane bending, while aromatic C-H out of plane bending explains the peaks about 900-650 cm^{-1}. After the adsorption process of both MG and MO dyes, the intensity of the peaks was less and that corresponds to the interactions that might be present between the functional groups in MIL-53(Al) and both dyes. Moreover, appearance of a new adsorption peak at 1150 cm^{-1} after adsorption of MG can be attributed to the presence of MG on the surface of the MOF. Also, the increase in intensity of the peak at 1750 cm^{-1} can be assigned to carboxylic stretching and the ligand-Al bond vibration. After adsorption of MO, a decrease in intensity in some of the peaks in the range of 450 to 1650 cm^{-1} is related to the hydrogen bond interaction between the OH group and MO.

Adsorption Experiments

Removal Efficiencies

A comparison of the removal efficiency of MIL-53(Al) for both dyes in single-dye solution and binary-dye solution as a function of time is represented in Fig. 3.

The removal efficiency of MO reached up to 99.5% within the first 10 minutes whereas, it reached 88.9% when MG was introduced as a competing solute as shown in Figure 3a. Similarly, it was observed that MIL-53 behaved better in removing MG as a single solute opposing to binary mixture of MO and MG as shown in Figure3b. It can be seen that in 30 min, MG was completely removed in the single-dye solution, while when being mixed with MO, the adsorption took 180 min to remove most of the dye (98.5%).

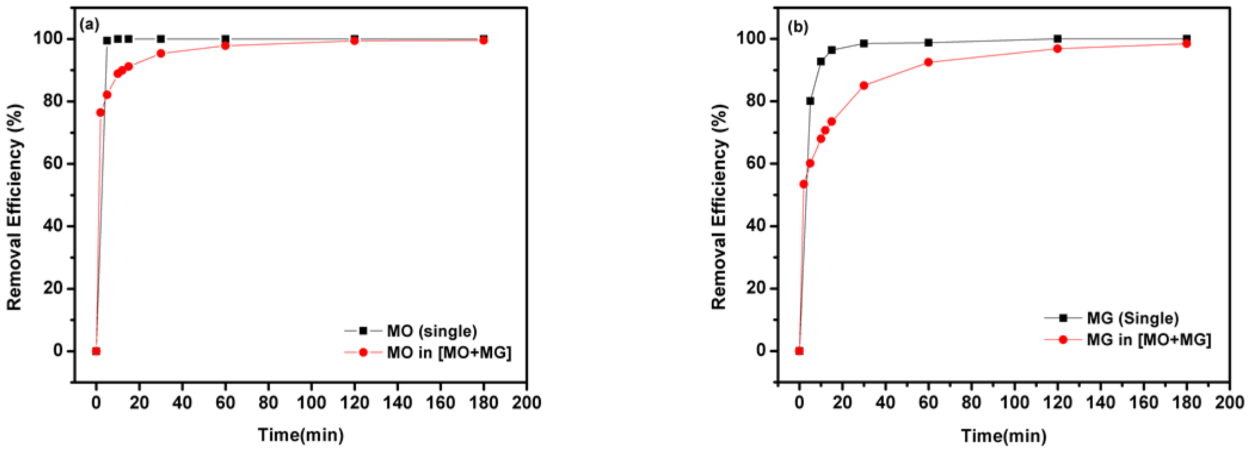

Fig. 3 Comparison of (a) MO removal efficiency and (b) MG removal efficiency onto MIL-53(Al) in single and binary-dye solutions at an initial concentration of 13 mg/L for both dyes and 50 mg MOF. The contact time was 180 min and the pH was 6. The stirring speed was 100 rpm. The temperature was 25°C.

A comparison between the percentage removals of each dye suggests that the removal of MO was always greater than that of MG in both single and binary-dye solutions. This indicates that MIL-53(Al) has a higher affinity for MO than for MG. In addition, a competitive behavior between MO and MG explains the lower removal efficiencies of MO and MG in binary-dye solution than those in single-dye solution.

pH effect and adsorption mechanism

The dye solution's initial pH is one of the significant factors that affect the adsorption process, precisely the adsorption capacity. The effect of pH on the adsorption capacity was examined up to an initial pH value of 10 since MG dye hydrolyzes in basic solution [15]. In this study, the adsorption capacities of MG and MO on MIL-53(Al) were determined at room temperature (25ºC) after reaching equilibrium (60 min). The range of initial pH used to perform the adsorption experiments was 2-10. The dye solutions had an initial concentration of 7 mg L^{-1} and the amount of adsorbent added was 10 mg of MIL-53(Al). Fig. 4a demonstrates the effect of pH on MG and MO adsorption. When pH values were increased from 2 to 6, the adsorption capacity of both MG and MO increased as a result. It can be seen that MG and MO had the maximum adsorption capacities of 39.03 and 43.18 mg/g, respectively at a pH value of 6, which is the natural pH of both dyes. On the other hand, the adsorption capacities of both dyes decreased at pH ≥8. This could be due to the breakdown of MIL-53(Al) structure in alkaline solution [16].

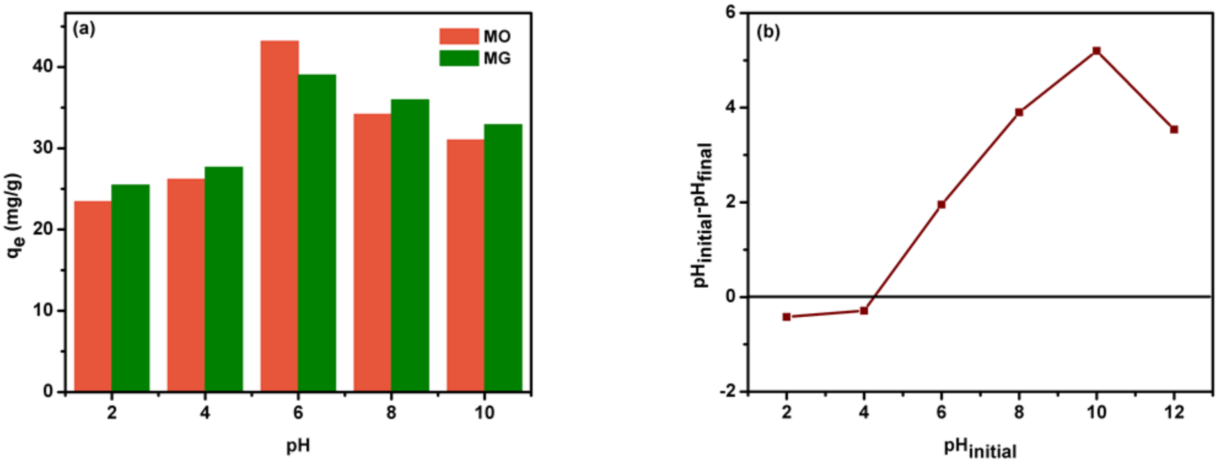

Fig. 4 (a) Effect of solution pH on the adsorbed amount of MO and MG over MIL-53(Al); (b) Determination of MIL-53(Al) point of zero charge by plotting ΔpH vs. initial pH. The contact time was 180 min. The stirring speed was 100 rpm. The temperature was 25°C. Dosage was 10 mg and Co for both dyes was 7 mg/L.

In order to understand and explain the effect of pH on the adsorption performance of MIL-53, point of zero charge (PH_{PZC}) plot was constructed as shown in Fig. 4b. Accordingly, the pH_{PZC} was found to be at 4.4 pH. When pH is less than pH_{PZC} (4.4), the charge of the surface of the MOF is positive. This should contribute to the adsorption of the anionic dye MO, which is negatively charged on MIL-53(Al) by electrostatic interaction. However, the adsorption capacity of this dye on the adsorbent was found to be relatively low as given by the experimental data, which may suggest that the adsorption capacity of MIL-53(Al) to MO was not mainly controlled by the electrostatic interaction. The fact that the adsorption capacity increased when the pH of solution increased from 2 to 4 suggests that some other mechanism can be controlling the adsorption like hydrogen bond interaction or π-π stacking interactions. Studies showed that MIL-53(Al) has a 3D structure that has the ability to alter the dimensions of porous channel after the absorption of polar and hydrocarbon molecules. This alteration is known as the breathing effect of the MOF [22], [23]. In other words, narrow pores replace the large pores on which the guest molecules were adsorbed and taken out, after which they go back to their large forms with the increase in the cover degree. The mechanism that the adsorption followed can be explained as follows. Many hydrated protons (H_3O+) were attracted to the negatively charged surface of MIL-53(AL) in the solution. The breathing effect made it possible for H_3O+ to enter into the MOF's structure, but not MO, although both have larger kinetic diameters than that of MIL-53(Al), especially MO which had a very large volume [23]. Furthermore, H_3O+ neutralized the negatively charged MOF, which resulted in weak electrostatic interaction between the dye and the MOF, and thus reducing the adsorption capacities for the dye. Moreover, the dye has a benzene ring that may accumulate with the MOF's phthalic acid unit through π-π stacking [24]. In this work, this kind of interaction didn't have the same effect as the hydrogen bonding did, which explains the decrease in the adsorption capacities of the dyes.

On the other hand, since MG is a cationic dye that is positively charged, less amounts of this dye will be adsorbed due to the electrostatic repulsion between MG and the adsorbent, which explains the experimental results and can be seen in Fig. 4a. When pH is higher than pH_{PZC}, the MOF will be negatively charged. This is the case when pH is equal to 6, 8, and 10 in Fig. 4a. The adsorption capacities of both dyes are higher than those obtained in low pH solutions. The electrostatic interaction between the positively charged MG and the MOF clearly explains this phenomenon. However, in the case of the negatively charged anionic dye MO, which should become less adsorbed due to the electrostatic repulsion, an opposite behavior was observed. This can be due to the damage that has happened to the structure of MIL-53(Al) in basic solution and the hydrolysis of MO in basic solution that may transform it into another compound. Therefore, the adsorption of MO and MG on MIL-53(Al) can be explained by the adsorption mechanisms of electrostatic, hydrogen bond and π-π stacking interactions between the dyes and the MOF.

Effect of initial concentration

The initial concentration of a dye is one of the parameters that have a significant influence on the amount of dye being adsorbed. The effect of initial concentration of MG and MO on the removal efficiency of MIL-53(Al) is shown in Fig. 5 and 6, respectively.

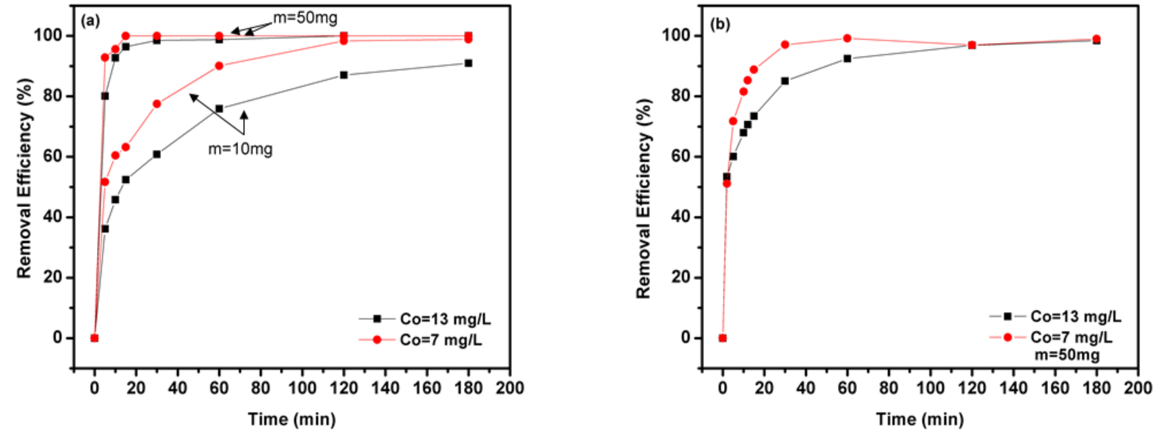

Fig. 5 Effect of initial concentration on the adsorbed amount of MG in (a) single-dye solution and (b) binary-dye solution. The contact time was 180 min. The stirring speed was 100 rpm. The temperature was 25°C.

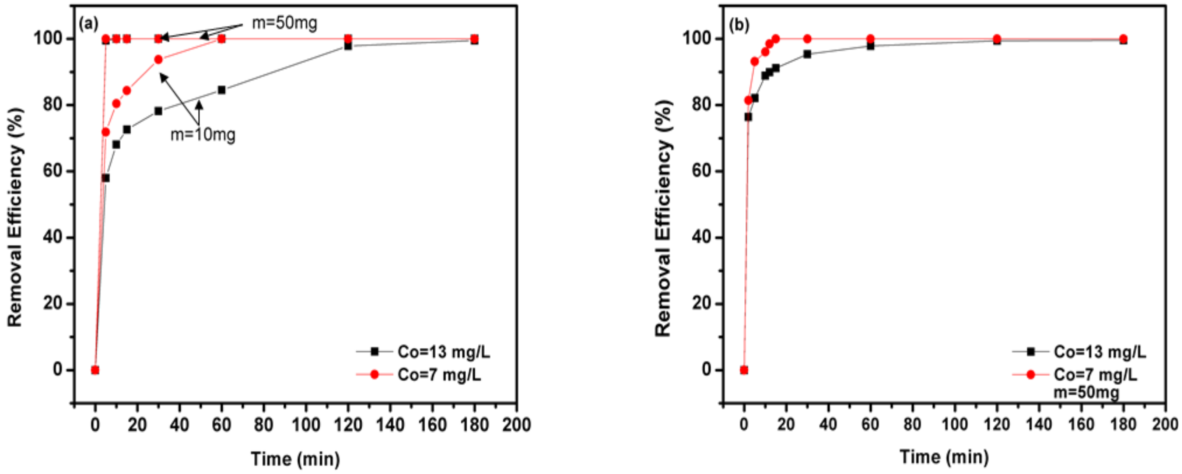

Fig. 6 Effect of initial concentration on the adsorbed amount of MO in (a) single dye solution and (b) binary-dye solution. The contact time was 180 min. The stirring speed was 100 rpm. The temperature was 25°C.

The results demonstrated are obtained from both single and binary-dye solutions. It can be seen that an increase in MG initial concentration from 7 mg/L to 13 mg/L at a fixed amount of 50 mg or 10 mg of MOF leads to a decrease in the percentage removal of that dye in both single and binary solutions during a period of 3h. This finding can be attributed to the saturation of the available adsorption sites on the MOFs surface. However, the adsorption capacity of the MOF will increase as a result of increasing the initial concentration of the dye. This is because of the mass transfer between the dye and MOF, which require higher driving force at higher initial concentration of the dye [16]. In addition to that, adsorption capacity is defined as the amount of adsorbate (mg) per amount of adsorbent (g) (mg/g) which will be higher as the initial concentration of the dye increases per the same amount of adsorbent. On the other hand, two behaviors were noticed for the adsorption of MO in the single-dye solution. It remained intact with the increase of MO initial concentration when 50 mg of MOF was added, as 100% removal efficiency was achieved in 5 minutes at both concentrations, while when a dosage of 10 mg was used, a similar behavior to that obtained with MG was shown, as an increase in MO initial concentration led to a decrease in the percentage removal . The concentration-independent adsorption was not the case when studying the removal of MO from the binary solution as it had a similar behavior to that of MG when 50 mg of MOF was used.

Effect of amount of MOF

Another factor that affects the adsorption process is the dosage of the adsorbent being added to the dye solution. Fig. 7 and 8 and show the effect of MOF dosage on its removal efficiency of MO and MG dyes, respectively.

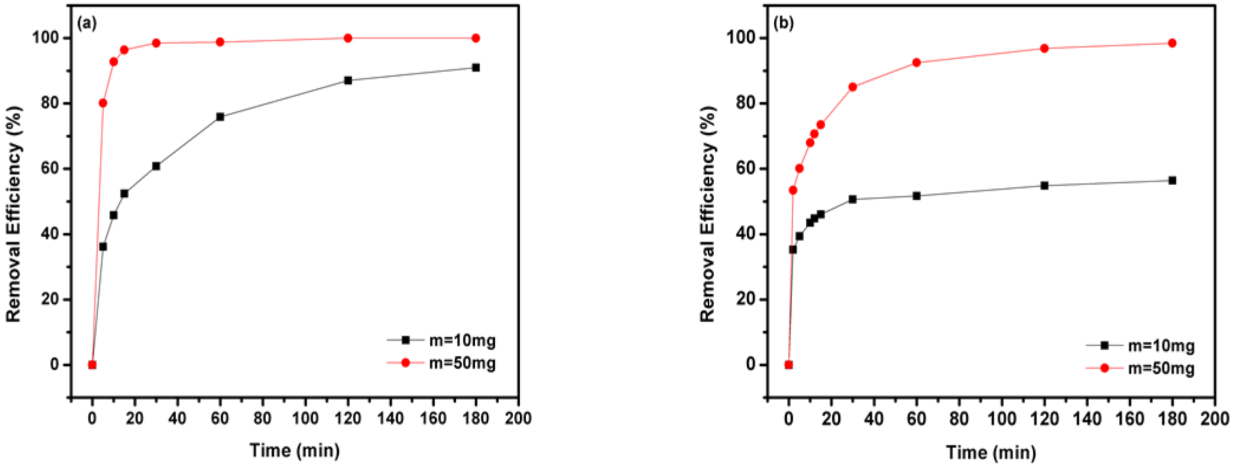

Fig. 7 Effect of MIL-53(Al) dosage on the adsorbed amount of MG in (a) single dye solution and (b) binary-dye solution at an initial concentration of 13 mg/L. The contact time was 180 min. The stirring speed was 100 rpm. The temperature was 25°C.

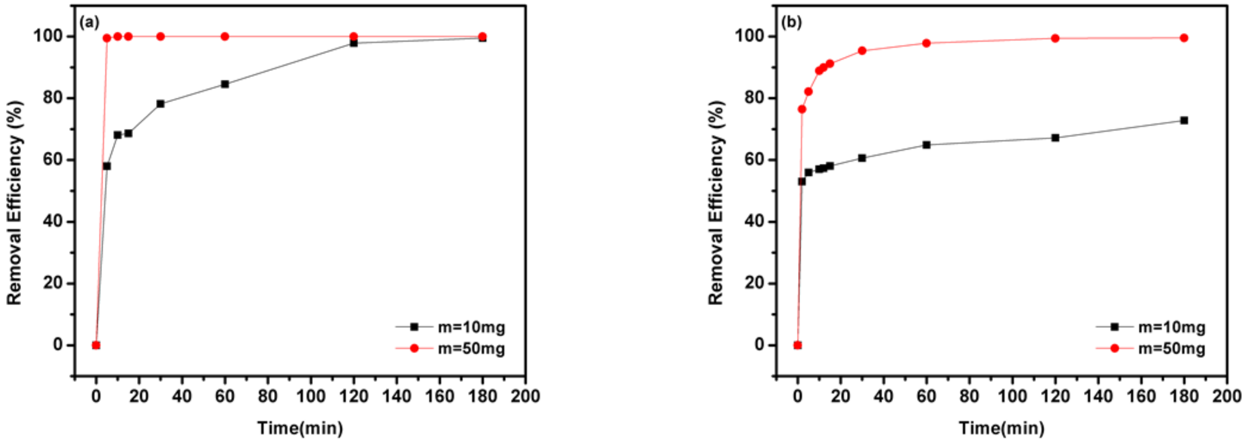

Fig. 8 Effect of MIL-53(Al) dosage on the adsorbed amount of MO in (a) single dye solution and (b) binary-dye solution at an initial concentration of 13 mg/L. The contact time was 180 min. The stirring speed was 100 rpm. The temperature was 25°C.

The initial dye concentration was fixed at 13 mg/L in which an amount of 10 or 50 mg of MIL-53(Al) was added to carry out the experiments at room temperature. It can be seen that the percentage removal of both dyes whether in a single or a binary-dye solution when using an amount of 50 mg of MOF was higher than that when 10 mg of MOF was used during a period of 3h. This indicates that the higher the amount of MOF added, the higher the percentage of dye removal. This can be explained based on the fact that more MOFs mean more active sites available for adsorption hence increasing the amount of dye adsorbed [25]. This also explains the decrease in the adsorption capacity when increasing the MOF dosage.

Adsorption kinetics

Kinetic models are defined by using the controlling techniques of adsorption like diffusion control, chemical reaction or mass transfer coefficient. When it comes to selecting the finest modes of operation for the full-scale adsorption approach, the kinetics of dye adsorption onto adsorbent substances is an essential requirement. When coming up with the adsorption system, it is essential to take this rate into account, which can be calculated from the kinetic study. The solute uptake rate is demonstrated by the kinetics study and can be clearly used for controlling the dye's residence time at the mixture interface. Therefore, various kinetic models were used to study the MO and MG kinetics onto MOF MIL-53(Al). The same procedure described earlier was used here. At certain time intervals, samples were taken from the solutions that had initial concentrations of 7-13 mg/L in order to determine the concentrations of MO and MG with time.

Three kinetic models were used to investigate the data. The pseudo first-order (PFO) model [26], the pseudo second-order (PSO) model [27], and elovich model [28] were studied in this work and can be demonstrated by equations (4-6).

Pseudo first-order model

$$q_t = q_e(1 - e^{-k_1 t}) \tag{4}$$

Pseudo second-order model

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{5}$$

Elovich model

$$q_t = \frac{1}{\beta} \ln(1 + \alpha\beta t) \tag{6}$$

Where q_e and q_t (mg.g^{-1}) are the adsorption capacity of MG or MO at equilibrium and at specific time t (min), respectively, k_1 (min^{-1}) represents the rate constant of the first-order kinetic , k_2 (g.mg^{-1}.min^{-1}) is the second-order kinetic constant, α (mg.g^{-1}.min^{-1}) is the initial adsorption rate, and β (g.mg^{-1}) is a desorption constant associated to the degree of covered surface and the chemisorption activation energy. Non-linear regression was used to find out the kinetic parameters.

The kinetic parameters and R^2 values for MO and MG adsorption are presented in Table 1 and 2, respectively. It can be seen that MG adsorption over MIL-53(Al) follows a PSO model, whether it was present in a single or binary-dye solution. On the other hand, the adsorption of MO in a single dye solution followed both PFO and PSO models, while the PSO model provided the best fit for the data in the case of a binary-dye solution. Therefore, it can be proposed that MG and MO adsorption are most likely controlled by chemisorption as the rate-limiting step [29]. Moreover, Fig. 9 demonstrates the plots of q_t versus t obtained from the PSO model for both MO and MG dyes in single and binary solutions.

Table 1 Kinetic parameters for MO adsorption in single and binary-dye solutions

Type of MO Solution	Kinetic Model	Kinetic Parameters	Initial Concentration, C_o (mg/L)	
			7	13
		q_e (exp) (mg.g^{-1})	5.551	8.153
Single Dye Solution	PFO	k_1 (min^{-1})	2.352	8.962
		q_e (cal) (mg.g^{-1})	5.551	8.146
		R^2	1.000	1.000
	PSO	k_2 (g.mg^{-1}.min^{-1})	5.834	4.886
		q_e (cal) (mg.g^{-1})	5.551	8.159
		R^2	1.000	1.000
	Elovich	α(mg.g^{-1}.min^{-1}) $\times 10^{10}$	1.611	4.934
		β(g.mg^{-1})	5.160	3.609
		R^2	0.985	0.987
Binary-Dye Solution [MG+MO]	PFO	q_e (exp) (mg.g^{-1})	7.015	12.899
		k_1 (min^{-1})	0.847	0.786
		q_e (cal) (mg.g^{-1})	6.926	12.120
		R^2	0.996	0.971
	PSO	k_2 (g.mg^{-1}.min^{-1})	0.301	0.118
		q_e (cal) (mg.g^{-1})	7.103	12.620
		R^2	0.999	0.996
	Elovich	α(mg.g^{-1}.min^{-1})	1.587×10^{10}	1.265×10^{6}
		β(g.mg^{-1})	4.124	1.479
		R^2	0.986	0.993

Table 2 Kinetic parameters for MG adsorption in single and binary-dye solutions

Type of MO Solution	Kinetic Model	Kinetic Parameters	Initial Concentration, C_o (mg/L)	
			7	13
		q_e (exp) (mg.g^{-1})	7.892	14.397
Single Dye Solution	PFO	k_1 (min^{-1})	0.530	0.324
		q_e (cal) (mg.g^{-1})	7.848	14.200
		R^2	0.998	0.998
	PSO	k_2 (g.mg^{-1}.min^{-1})	0.299	0.057
		q_e (cal) (mg.g^{-1})	7.958	14.640
		R^2	0.999	0.999
	Elovich	α(mg.g^{-1}.min^{-1}) $\times 10^{10}$	3.674×1010	4.247×107
		β(g.mg^{-1})	3.751	1.565
		R^2	0.994	0.988
Binary-Dye Solution [MG+MO]	PFO	q_e (exp) (mg.g^{-1})	6.992	13.157
		k_1 (min^{-1})	0.309	0.257
		q_e (cal) (mg.g^{-1})	6.640	11.550
		R^2	0.970	0.861
	PSO	k_2 (g.mg^{-1}.min^{-1})	0.0704	0.0145
		q_e (cal) (mg.g^{-1})	7.104	13.450
		R^2	0.997	0.999
	Elovich	α(mg.g^{-1}.min^{-1})	221.5	83.460
		β(g.mg^{-1})	1.455	0.681
		R^2	0.956	0.995

When using the PSO model, the calculated values of q_e are similar to the experimental values for both dyes, whether in a single or binary- dye solution. The PSO rate constant (k_2) was found to decrease when increasing the initial concentration of MO and MG dyes from 7 to 13 mg/L. This can be due to the increase in the competition for available sites on the surface of the MOF [30], [31]. Moreover, the rate constants for MO adsorption were higher than the ones obtained for MG adsorption, agreeing with the greater removal efficiency of MIL-53(Al) for MO dye.

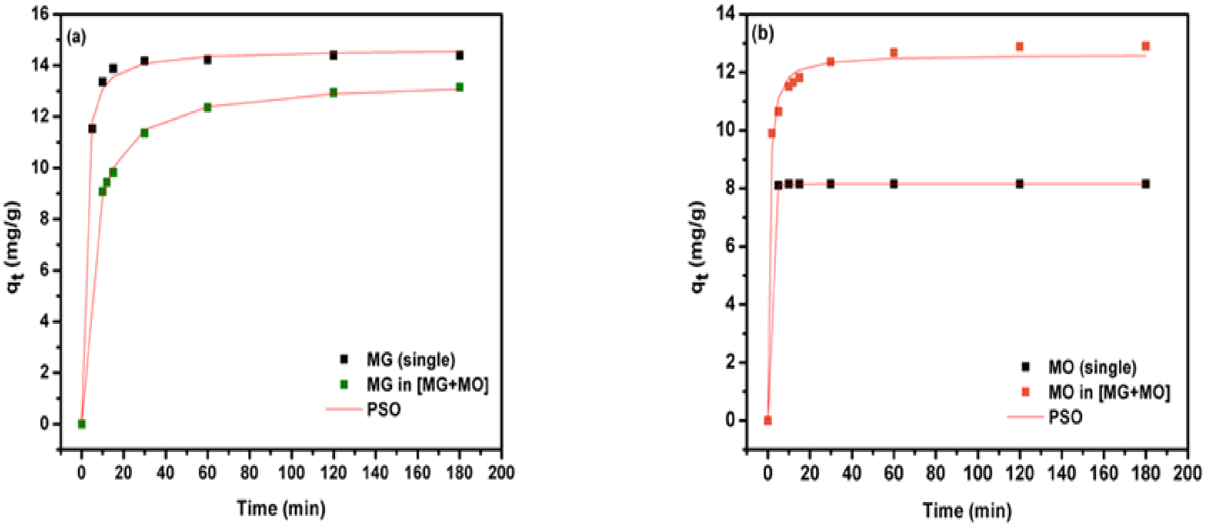

Fig. 9 PSO models for the removal of (a) MG and (b) MO in single and binary solutions at an initial concentration of 13 mg/L and 50 mg of MOF. The contact time was 180 min and pH was 6. The stirring speed was 100 rpm. The temperature was 25°C.

Adsorption isotherms

The adsorption isotherm is crucial for the clarification of the interaction between the adsorbent and adsorbate and to give an overall idea of the adsorption capacity. The isotherm models play a huge part in comprehending the adsorption mechanism. The surface phase can be either monolayer or multilayer [32]. It is crucial to report the adsorption process using the most proper model by fitting the isotherm data to various isotherm models. The isotherm experiments were carried out in 50-mL conical flasks containing 50 mL of MO or MG solution with initial concentration ranging from 13 to 250 mg/L, which were sealed and maintained at 25, 35 or 65 ºC before the addition of 10 mg of MIL-53(Al). Langmuir [33] and Freundlich [33] were the models that were used to analyze the experimental data.

The Langmuir model is developed on the assumption that homogeneous sites of the adsorbent will be covered with a monolayer of the adsorbate, in which the adsorbed molecules don't interact with each other [34]. This model is described by equation (7).

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{7}$$

Where q_m is the maximum adsorption capacity when the adsorbates are completely covering the monolayer surface (mg/g), and K_L is the Langmuir constant (L/mg) linked to the adsorption energy (L/mg).

The Freundlich isotherm assumes a heterogeneous and multilayer adsorption [33]. The surface on which the adsorption takes place is considered to have different accessible sites with various adsorption energies [32].

The Freundlich isotherm is given by equation (8).

$$q_e = k_F C_e^{\frac{1}{n}} \tag{8}$$

Where k_F is the Freundlich constant associated with the adsorbent capacity $((\mathrm{mg.g^{-1}})(\mathrm{L.mg^{-1}})^{1/n})$ and n represents the intensity of the adsorption driving force. The higher the value of n, the higher the adsorption feasibility. Since Freundlich isotherm considers both monolayer and multilayer adsorption, both chemical and physical adsorption have to be accounted when using this model [15].

The nonlinear fittings of Freundlich isotherm of MG and MO in single dye solution at 25° with 10 mg of MOF are plotted in Fig. 10.

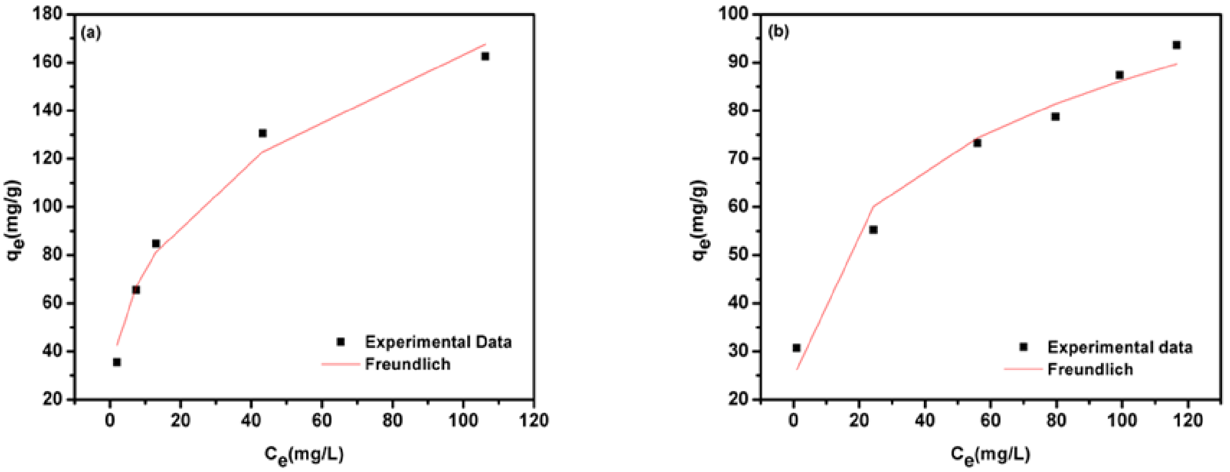

Fig. 10 Freundlich model for the removal of (a) MG and (b) MO in single dye solutions with 10 mg of MOF at 298 K. The contact time was 180 min and the pH was 6. The stirring speed was 100 rpm.

As can be seen from the plots, increasing the initial concentrations of both dyes results in a considerable increase in the adsorption capacities. A similar behavior was observed at all other temperatures of 35, 45 and 65ºC at a range of initial concentration up to 120 mg/L. This can be attributed to the enhancement of collision between the dyes and the MOF caused by the increase of the initial concentration.

The isotherm parameters computed according to Langmuir and Freundlich models together with the R^2 values are provided in Table 10. This table indicates that the data are best fitted using the Freundlich isotherm model for both MG and MO. This implies that the adsorption of MG and MO into MIL-53(Al) is controlled by a multilayer adsorption [35]. Hence, this model assumes both chemical and physical adsorption. n value was higher than 1 at all temperatures for both dyes, which indicates the favorability of the adsorption process, MIL-53(Al) has affinity to both anionic and cationic dyes [26], and that the adsorption is heterogeneous.

Table 3 Adsorption isotherm parameters of single dye adsorption by MIL-53(Al) at various temperatures

Dyes	**Isotherm Model**	**Isotherm Parameters**	**Temperature (K)**			
			298	**308**	**318**	**338**
MO	**Langmuir model**	**K_L (L.mg^{-1})**	0.078	0.128	0.138	0.224
		q_m (mg.g^{-1})	176.6	182.5	208.3	219.4
		R^2	0.979	0.869	0.876	0.946
	Freundlich model	**K_F (mg.g^{-1})(L.mg^{-1})$^{1/n}$**	33.520	47.200	60.360	67.62
		n	2.899	3.408	3.845	3.858
		R^2	0.986	0.999	0.990	0.967
MG	**Langmuir model**	**K_L (L.mg^{-1})**	0.472	0.035	0.045	0.089
		q_m (mg.g^{-1})	81.2	134.3	143.5	128.8
		R^2	0.745	0.660	0.815	0.929
	Freundlich model	**K_F (mg.g^{-1})(L.mg^{-1})$^{1/n}$**	26.560	40.350	28.36	46.62
		n	3.910	5.049	3.210	5.029
		R^2	0.974	0.900	0.900	0.986

Adsorption Thermodynamics

Temperature dependent adsorption isotherms are used to identify the thermodynamics parameters in order to study the adsorption process. They determine the relationship between the adsorbent and the adsorbate and indicate the practicality and spontaneous nature of the adsorption mechanism. The adsorption data of MG and MO on MIL-53(Al) at different temperatures were used to calculate Gibbs free energy ($\Delta G°, kJ/mol$), standard enthalpy ($\Delta H°, kJ/mol$), and standard entropy ($\Delta S°, J/mol\ K$) according to the following formulas (9) and (10).

$$\Delta G° = -RTln(K_{eq}) \tag{9}$$

$$ln(K_{eq}) = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{10}$$

Where R is the universal gas constant, and K_{eq} is the thermodynamic equilibrium constant.

Based on the MG and MO adsorption isotherm data, the value of $\ln(K_{eq})$ at a specific temperature is calculated by graphing a plot of $\ln(q_e/C_e)$ against q_e and extrapolating q_e to zero [36]. Equation 9 was used to compute the adsorption free energy change (ΔG^o). By plotting $\ln(K_{eq})$ against 1/T, the change in enthalpy(ΔH^o) and entropy (ΔS^o) for MG and MO adsorption were determined from the slope and intercept of the linear Van't Hoff plot shown in Fig. 11. These obtained thermodynamics parameters are presented in Table 4. The negative values of the Gibbs free energy change (ΔG^o) for both dyes suggest the spontaneous nature of the adsorption process. When increasing the temperature, the values of (ΔG^o) decrease, which accounts for a drop in the probability of adsorption at greater temperatures. Furthermore, it can be seen that ΔG^o values for MO are more negative than those of MG, suggesting more favorability to the adsorption of MO onto MIL-53(Al) [18], which is in good agreement with the obtained results. According to literature, if ΔG^o is between -20-0 kJ/mol, the adsorption is physical, whereas it is considered chemical if it is between -400 to -80 kJ/mol. The range of ΔG^o values in this study indicate that the adsorption is not a solely chemical or physical adsorption, but a little bit of both [15]. Positive values of the change in enthalpy (ΔH^o) were found for the adsorption of both dyes on MIL-53(Al). This indicates that the adsorption process is endothermic. The entropy change (ΔS^o) was also found to be positive for both dyes, which suggests that the randomness of the dye at the MOF-solution interface increased. This happened because the water molecules were desorbed from the surface of the MOF [37].

Table 4 Thermodynamic parameters of MO and MG adsorption by MIL-53(Al)

Dyes	**ΔG^o (kJ.mol^{-1})**				**ΔH^o (kJ.mol^{-1})**	**ΔS^o (J.mol^{-1}.K^{-1})**
	298 K	**308 K**	**318 K**	**338 K**		
MO	-35.35	-37.81	-39.25	-43.08	22.18	193.11
MG	-34.55	-37.21	-36.02	-40.16	27.22	199.24

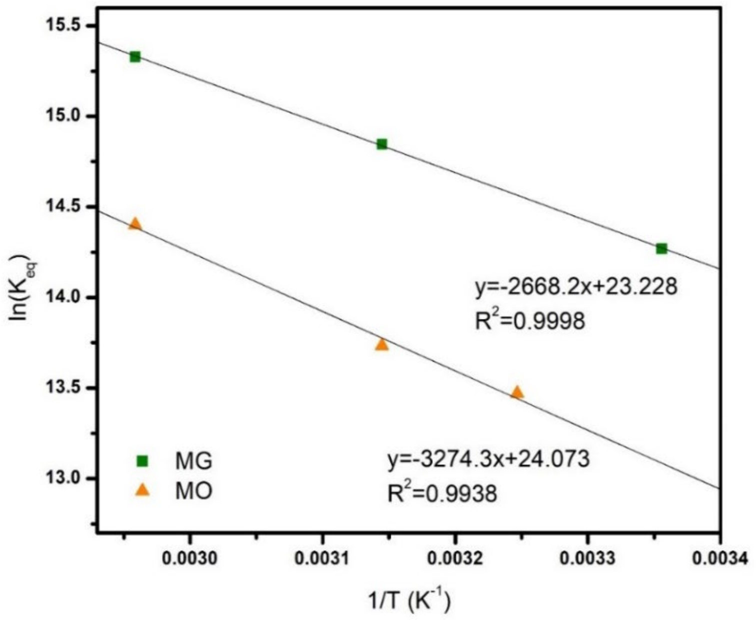

Fig. 11 Van't Hoff plot for ΔH^o and ΔS^o measurement of MO and MG adsorption on MIL-53(Al).

Selectivity of binary-dye adsorption

Table 5 shows the adsorption selectivity for binary-dye solutions at initial concentrations of 7 and 13 mg.L^{-1} with addition of 10 or 50 mg of MIL-53(Al). The selectivity was calculated using Equation (3) by choosing Methyl Orange as dye 1 and Malachite Green as dye 2. The selectivity was always higher than 1, which indicates that MIL-53(Al) has a higher affinity for MO than for MG. Fig. 12 represents the effect of initial concentration on the selectivity at fixed amounts of MOF. It can be seen from the figure that the selectivity decreases with the increase of the initial concentration of the dyes at a fixed amount of MOF. This finding can be attributed to the saturation of the available adsorption sites on the MOF's surface. On the other hand, increasing the amount of MOF added to the solution results in increasing the selectivity at a fixed initial concentration. This is due to the fact that more active sites are available for adsorption hence increasing the adsorbed amount of the favorable dye (MO). These results agree with the high removal efficiencies at lower initial concentrations and higher amount of dosage. Therefore, selective adsorption of MO is favorable at these operating conditions.

Table 5 Selectivity at different initial concentrations and MOF dosage

MOF Dosage (mg)	**Initial Concentration, (mg.L^{-1})**	
	7	**13**
10	4.438	2.067
50	13.582	3.412

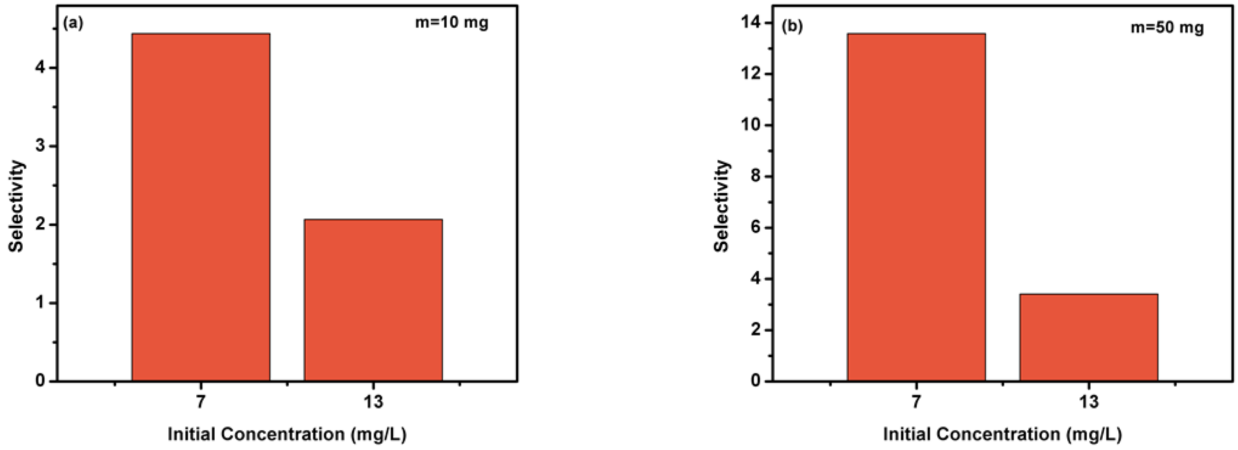

Fig. 12 Adsorption selectivity for binary-dye solutions at initial concentrations of 7 and 13 mg. L^{-1} with addition of (a) 10 and (b) 50 mg of MIL-53(Al). The contact time was 180 min and the pH was 6. The stirring speed was 100 rpm. The temperature was 25°C.

To further study the competitive behavior of the adsorption of MO and MG, the effect of the initial concentration of MG on the selectivity of MO in binary-dye solutions was examined. The experiments were performed by keeping the initial concentration of MO constant at 15 mg/L while altering the initial concentration of MG from 5 to 25 mg/L at a fixed amount of 10 mg of MOF. Figure 13 shows that as the initial concentration of MG increases, the selectivity of MO decreases due to the saturation of the available adsorption sites on the MOF's surface. However, the selectivity was always more than 1, which supports the fact that MIL-53(Al) has a higher affinity for MO than for MG even at higher initial concentrations of MG than those of MO.

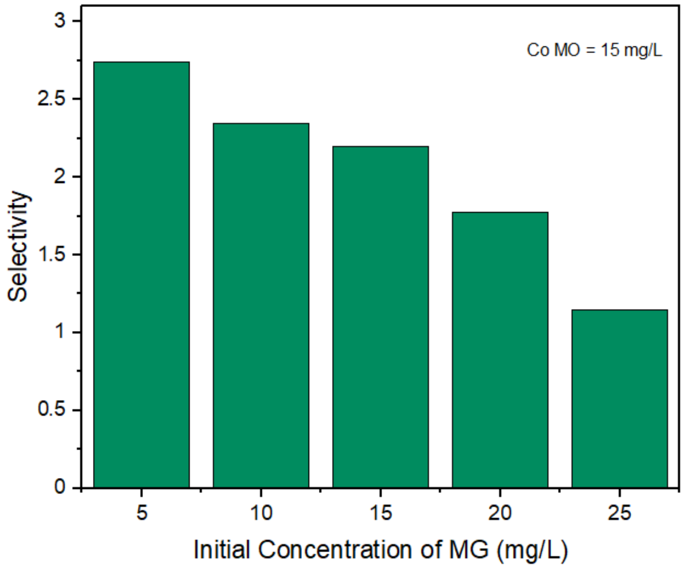

Fig. 13 Effect of MG on MO: Adsorption selectivity for binary-dye solutions at a constant MO initial concentration of 15 mg. L^{-1} with addition of 10 mg of MIL-53(Al). The contact time was 180 min and the pH was 6. The stirring speed was 100 rpm. The temperature was 25°C.

Regeneration of MIL-53(Al)

The ability to regenerate and reuse adsorbents can help in cost and dosage reduction when removing pollutants from wastewater in industrial processes, as they will be used for extended amount of time. To investigate the endurance of MIL-53(Al) over the long term, its reusability was examined in the binary-dye adsorption process. First, a MOF dosage of 50 mg was activated by washing it with 70% ethanol for 3h. Then, it was used for the removal of MO and MG in a binary-dye solution of an initial concentration of 13 mg/L. After the adsorption process, centrifugation was used to split up MIL-53(Al) particles from the liquid solution (4000 rpm for 2 min). Then, 70% ethanol was used to wash MIL-53(Al) from the adsorbed dyes. Finally, using an oven, the MOF was dried at 100º C and used for the next experiment.

Fig. 14represents the influence of the regeneration cycles on the adsorption capacity of MO and MG into MIL-53(Al). It can be seen that the adsorption capacity stayed intact as the recycle times increased, suggesting that this washing method for removing MO and MG dyes was a success. After the first-cycle regeneration, MIL-53(Al) still exhibited a comparable adsorption capacity, showing that the ethanol-washing was a feasible and effective technique to remove MG and MO from the spent MIL-53(Al). As the regeneration cycle increased, the adsorption capacity of MIL-53(Al) remained similar and no significant loss was observed. After four regeneration cycles, MIL-

53(Al) could still exhibit 99% of the original capacity of MIL-53(Al). This suggests that MIL-53(Al) can be readily and straightforward regenerated and the adsorption capacity can remain almost the same, even up to 4 cycles.

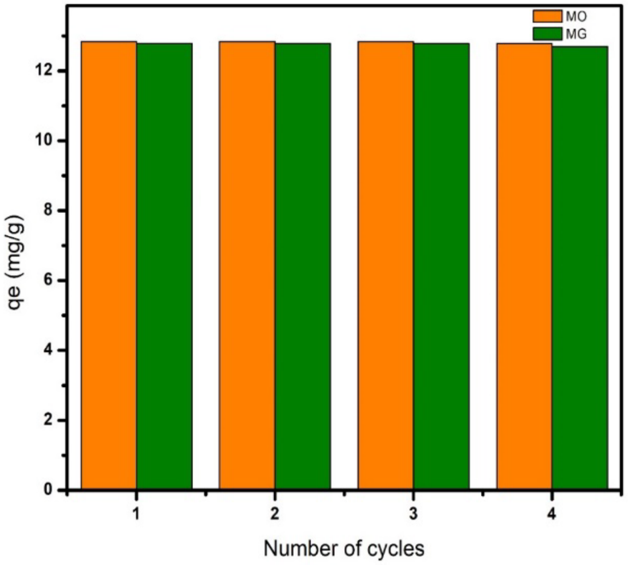

Fig. 14Effect of number of cycles of MIL-53(Al) on MG and MO binary adsorption at 298 K, $C_o = 13$ mg/L, and m=50 mg. The contact time was 180 min and the pH was 6. The stirring speed was 100 rpm.

The adsorption capacities of Malachite Green and Methyl Orange with various previously reported MOFs are demonstrated in Table 6. It can be seen that Al-based MOF (MIL-53(Al) exhibited a higher adsorption capacity for the removal of MO than Cr-based MOF (MIL-53(Cr) and an intermediate capacity among other reported MOFs. On the other hand, a less efficient performance was observed for the removal of MG compared to the reported MOFs in literature. This low capacity for MG removal can be explained by the competitive behaviour of the dyes since dual-dye solutions were used where selective adsorption of MO was found to be favorable.

Table 6 Comparison of adsorption capacities of MO and MG using various MOFs obtained in the present work and reported in the literature.

Dye	Adsorbent	q_m (mg/g)	Reference
MO	MIL-53(Cr)	57.9	[38]
	MIL-101(Cr)	114	[38]
	MOF-235	477	[39]
	MIL-68(Al)	341.3	[30]
	MIL-100(Cr)	211.8	[31]
	MIL-100(Fe)	1045.2	[31]
	NH_2-MIL-101(Al)	188	[40]
	MIL-53(Al)	182.5	**The present work**
MG	ZIF-67	2430	[41]
	Cu- MOF	38.01	[42]
	Cu-MOFs/Fe_3O_4	113.67	[43]
	MIL-100(Fe)	146	[44]
	MIL-53(Al)-NH_2	188.6	[15]
	MIL-100-SO_3H	528	[45]
	NH_2-MIL-101(Al)	274	[46]
	MIL-53(Al)	81.2	**The present work**

Conclusion

Adsorptive removal of cationic and anionic dyes from aqueous solutions using Metal Organic Framework (MOF) was investigated in this study. Malachite Green (MG) and Methyl Orange (MO) were the dyes that were used as the model adsorbates, while MIL-53(Al) was the adsorbent of which performance was examined. Single and binary-dye solutions were prepared to carry out the batch adsorption experiments. Different factors were found to have an effect on the adsorption process such as MOF dosage, initial dye concentration, pH of the solution and temperature. In case of single-dye solutions, MO was completely removed from the solution within the first 5 minutes, while it took 15 minutes to remove MG at the optimum operating conditions. More time was needed to remove both dyes in binary-dye solutions at the same conditions due to the competitive behavior between MO and MG. MO was removed in 12 minutes, while 180 minutes were needed for MG to be completely adsorbed, indicating the selective adsorption of MO over MG. Pseudo-second order model was the model that the kinetics data followed with $R^2>0.996$ for both dyes. Isotherm data were best fitted to the Freundlich isotherm model for each of the dyes. The high adsorption behaviour of MIL-53(Al) is interpreted from hydrogen bonding and π-π stacking interactions between the dyes and the MOF surface. The adsorption of both kinds of dyes was found to be spontaneous and endothermic as indicated from the thermodynamics parameters ($\Delta G°, \Delta H°, \Delta S°$). The selectivity test for an equimolar binary-dye solution containing both MG and MO suggested the higher affinity of MIL-53(Al) towards MO over MG, as it reached a value of 13.582 at an initial concentration of 7 mg/L and 50 mg of MOF. Regeneration of MIL-53(Al) was possible by washing it with 70% ethanol and reusing it for over 4 cycles of adsorption-desorption with almost no reduction in the adsorption capacity. Accordingly, this study shows that Al-based MOFs, especially MIL-53(Al), has the ability to become a promising candidate for the removal of a diversity of azo dyes.

Acknowledgments

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