Removal of Methylene Blue by Iron Terephthalate Metal-Organic Framework/Polyacrylonitrile Membrane

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ABSTRACT: MIL-53(Fe)/PAN membrane is a mixture comprises iron terephthalate metal-organic framework on polyacrylonitrile, which were fabricated through the phase inversion method. The adsorption property of the MIL-53(Fe)/PAN was evaluated in batch condition over various concentration of methylene blue (MB) in water and without pH adjustment. The effect of MIL-53(Fe) to PAN ratio, initial MB concentration, and contact time to the degree of MB removal was investigated. This study reveals that as low as l g/L of the membrane with 1:5 of the MIL-53(Fe) to PAN ratio was capable of removing about 70% of the 15-ppm MB in 5 hours. The adsorption data, on the other hand, was best fit to the Freundlich isotherm and *pseudo*-first order kinetics models suggesting multilayer adsorption between the membrane and the MB with physisorption dominating the entire process. Hence, MIL-53(Fe)/PAN membrane is a potential material for environmental remediation and pollution control.

KEYWORDS: Adsorbent; adsorption; metal-organic framework; PAN membrane

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INTRODUCTION

Physical, chemical and biological methods are conventional water treatments methods to eliminate organic pollutants. Organic pollutants, such as organic dyes mostly have strong chemical bonding and functional groups to withstand decomposition and increase hydrophilicity (Tsai *et al*., 2007; Wang *et al*., 2014). Thus, dye pollutants are usually less amendable through the conventional techniques, especially biological and chemical approaches (Oliveira *et al*., 2012).

Metal-organic frameworks (MOFs) are porous solids comprise of metal nodes connected with organic linkers which are much larger than the oxygen linker in the inorganic porous solids, such as zeolites (Silva *et al*., 2010). MOFs become prominent due to their integration of semiconductivity, high crystallinity and tunable porosity that offer large interfacial surface areas, small electron-hole diffusion lengths which are the important characteristic of the material used for pollution control (Yaghi *et al*., 2003). Polyacrylonitrile (PAN) is a synthetic resin prepared by the polymerization of acrylonitrile. It is a hard and rigid thermoplastic material that is resistant to most solvents and chemicals. The wide popularity of PAN is results from their properties on chemical, thermal and mechanical and it is tolerance to most solvents and photo irradiation (Jain *et al*., 2012). Modification of PAN have brought wide applications with increasing strength and unique properties such as modified PAN with hydrazine to give smooth surface which enhance the adsorption of metal ions (Saed *et al*., 2012).

Membrane-based water treatment processes have become one of the most efficient and most reliable technologies. Recently, a study reported by Hinestroza and co-workers showed that immobilization Cu-BTC MOF (*a.k.a* MOF-199 or HKUST-1) on PAN nanofibers has the ability to remove the insecticide methyl parathion from the solution (Lange *et al*., 2014). This proves that both the PAN and MOF are the effective materials used in removing organic pollutants from solution. In this study, we demonstrate the adsorptive removal of methylene blue by MIL-53(Fe)/PAN membrane and also evaluate the effectiveness of MIL-53(Fe)/PAN membrane as the adsorbent in different adsorbent dose, contact time and initial methylene blue concentration.

METHODOLOGY

Reagent

Polyacrylonitrile (Mw = 150,000), terephthalic acid (BDC, 98%), and hydrofluoric acid, (HF, 49% in water), iron (III) chloride hexahydrate ($FeCl_3.6H_2O$), *N,N*-dimethylformamide (DMF) and methanol (CH_3OH) were purchased from Sigma-Aldrich and of analytical-reagent grade. All the chemicals and reagents were used as received and without any further purification or modification. Methylene blue (MB) from R&M was used as a model pollutant.

Preparation of MIL-53(Fe)/PAN membrane

MIL-53(Fe) was synthesized using the method used as reported by Munn *et al*., (2013). To prepare membrane with 1:5 of MIL-53(Fe) to PAN ratio, 0.1 g of MIL-53(Fe) was dissolved in 10 g of DMF solution. The mixture was sonicated for 5 minutes followed by addition of 0.5 g of PAN into the mixture solution. After vigorous stirring at room temperature for 12 hours, a homogenous solution formed. Subsequently, the mixture was transferred into a glass petri dish (Superior). The glass petri dish was put into an oven (115 V BD 23 Binder) at 80°C for 5 hours. Then, the glass petri dish was cooled down to room temperature naturally. 20 mL of deionized water was transferred into a glass petri dish for 1 hour, as detachable sample. Finally, the obtained MIL-53(Fe)/PAN membrane was taken from the glass petri dish and washed with deionized water for several times to remove any ionic residue, and then dried at room temperature for 24 hours (Bushell *et al*., 2012; Im *et al*., 2008; Yang *et al*., 2003).

Adsorption Study

MIL-53(Fe)/PAN membrane with 1:20, 1:10 and 1:5 ratio were studied. 0.5 g of the respective MIL-53(Fe)/PAN membrane was placed on the surface of MB solution (50 mL) with initial concentration of 5, 10, and 15 ppm, respectively. The adsorption of MB in water by MIL-53(Fe)/PAN membrane was investigated at room temperature and the degree of adsorption was evaluated, periodically, over a period of 540 minutes using the UV-Vis spectrophotometer (UV-Vis) (Carry 60, Agilent Technologies) at the wavelength of 665 nm. The percentage of adsorption MB in water by MIL-53(Fe)/PAN membrane were then be determined through following equation:

$$\text{Percent of MB Removal} = (A_o - A_t) / A_o \quad 100\% \tag{1}$$

where, A_o and A_t are initial absorbance of organic dyes at $t = 0$ and absorbance of organic dyes at t minutes, respectively. The amount of MB adsorbed at specific time interval can then be calculated using following equations:

$$\text{Amount of MB adsorbed, } mg{\cdot}g^{-1} = [\text{MB}]_t \times V / W \tag{2}$$

and

$$[\text{MB}]_t = [\text{MB}]_i \times \text{Percent of MB removal} \tag{3}$$

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where, $[MB]_i$ is the initial MB concentration at $t = 0$, $[MB]_t$ is the MB concentration at t minutes, V is the volume of MB solution in litre, and W is the weight of the membrane in gram.

RESULT AND DISCUSSION

Characterization of MIL-53(Fe)/PAN Membrane

Figure 1 shows SEM images of the synthesized MIL-53(Fe) and MIL-53(Fe)/PAN. The synthesized MIL-53(Fe) is predominated by the rod-like crystals as shown in Figure 1(a) where this observation is comparable to the findings reported by Ai *et al*., (2013) and Horcajada *et al.,* (2010). Figure 1(b) shows the morphology of MIL-53(Fe)/PAN membrane.

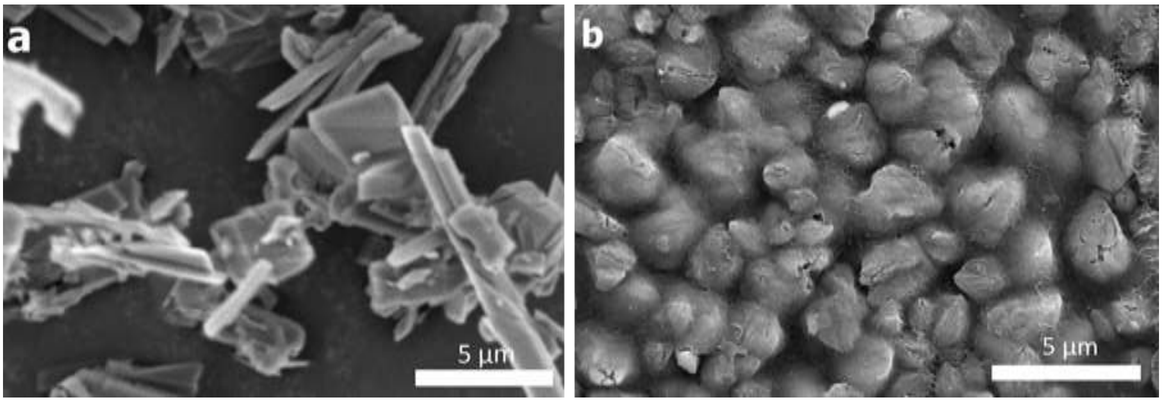

Figure 1. SEM images of (a) MIL-53(Fe) and (b) MIL-53(Fe)/PAN membrane.

The prepared MIL-53(Fe)/PAN membrane was analysed using the powder XRD and the XRD pattern was compared to that simulated and reference materials. Figure 2 confirms that the MIL-53(Fe) was successfully immobilized onto the PAN.

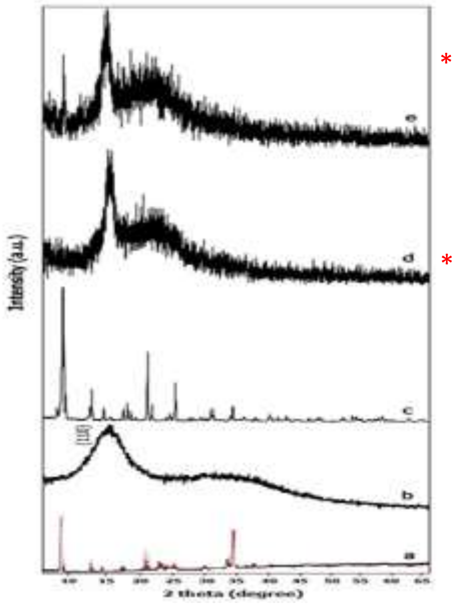

Figure 2. XRD patterns of (a) simulated MIL-53(Fe), (b) PAN reference peaks, (c) as-synthesized MIL-53(Fe), (d) as-prepared PAN membrane, and (e) MIL-53(Fe)/PAN membrane. Note that * shows the main peak for MIL-53(Fe).

Effect of MIL-53(Fe) to PAN Ratio

In this study the MIL-53(Fe) to PAN ratio where studied by changing the amount of MIL-53(Fe), *i.e.* 0.025, 0.05 and 0.1 g while the amount of PAN was fixed at 0.5 g. This gives 1:20, 1:10 and 1:5 of MIL-53(Fe) to PAN ratio. Figure 3 shows the relationship of the amount of filler or MIL-53(Fe) towards the adsorption of 5-ppm, 10-ppm, and 15-ppm MB in water by the MIL-53(Fe)/PAN membrane and for a period of 8 hours. The removal of MB from water increases with increasing amount of MIL-53(Fe), in which it can be attributed to the increasing adsorption sites on the surface of membrane (Mahmoodi *et al*., 2013). In other words, higher amount of MIL-53(Fe) in PAN is favourable for the removal of higher concentration of MB.

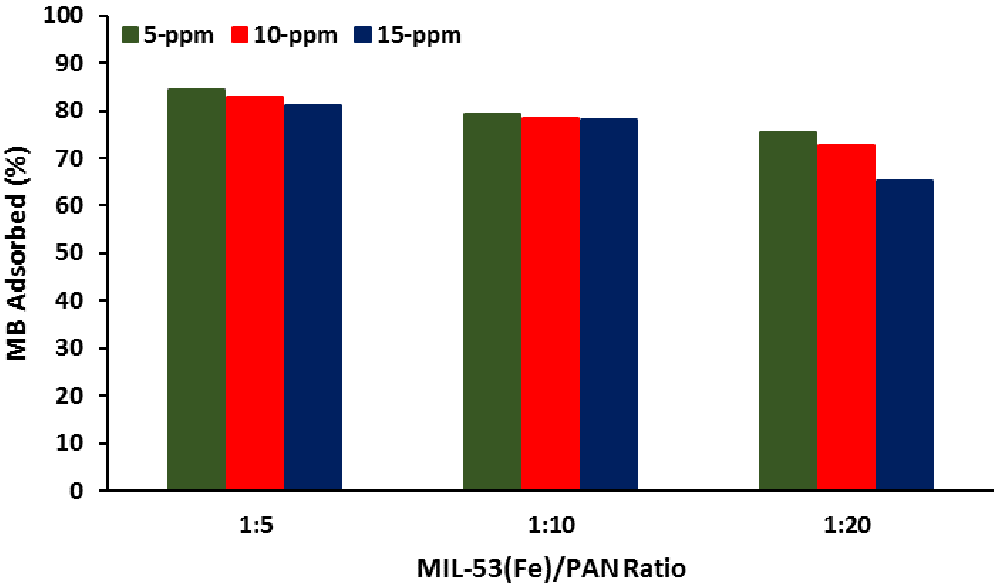

Figure 3. Effect of MIL-53(Fe)/PAN ratio on the removal of MB by MIL-53(Fe)/PAN membrane after 5 hours of contact time.

Effect of Initial MB Concentration

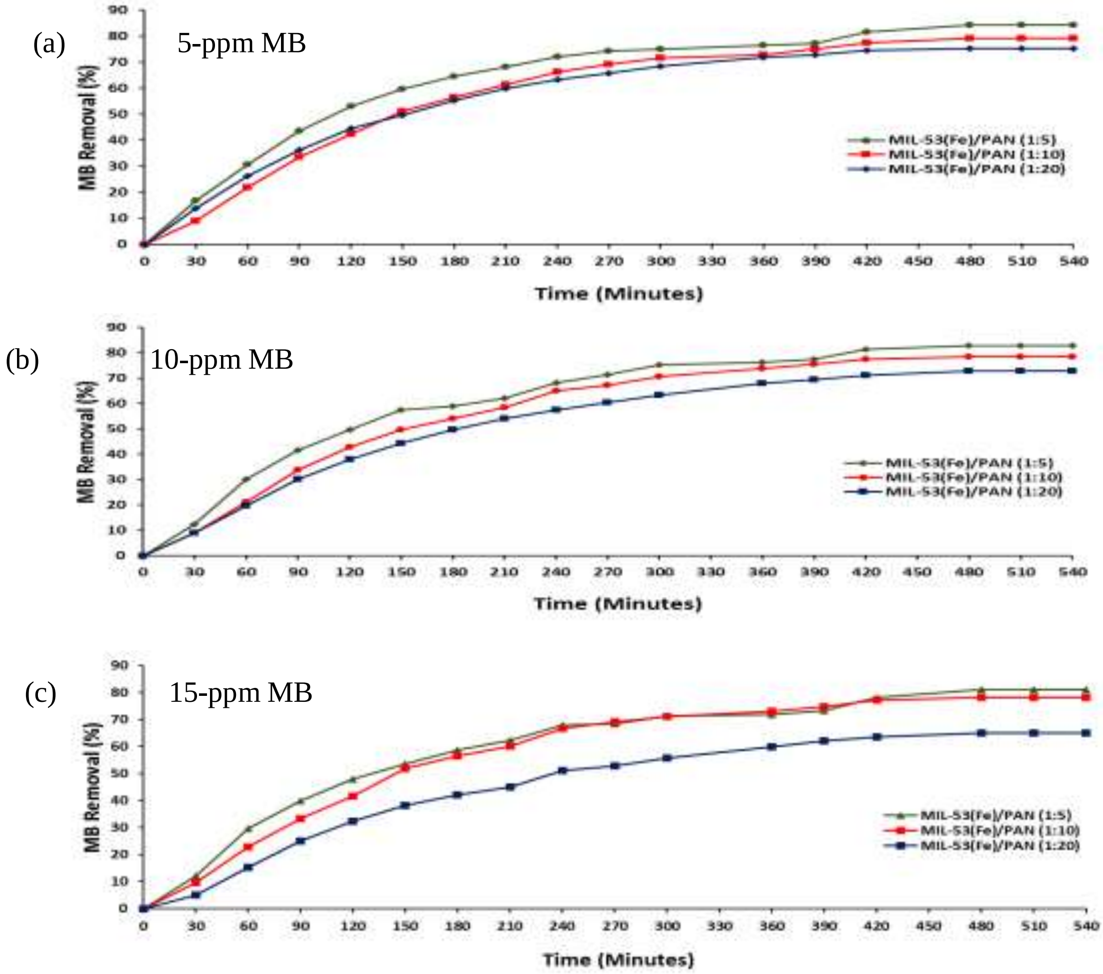

Figure 4. Effect of initial MB concentration (a) 5 ppm, (b) 10 ppm, and (c) 15 ppm towards adsorption capability of MIL-53(Fe)/PAN membrane in various ratios.

Figure 4 shows the adsorption capability of MIL-53(Fe)/PAN membrane prepared with different amount of MIL-53(Fe). The MIL-53(Fe)/PAN membrane with 1:20 ratio only capable of removing 75%, 72% and 65% of 5-ppm, 10-ppm, and 15-ppm MB, respectively, after 8 hours of contact time. However, the MIL-53(Fe)/PAN membrane with 1:5 ratio was able to adsorb 84%, 82% and 81% of 5-ppm, 10-ppm, and 15-ppm MB, respectively, in the same contact hours. The plots reveal that higher amount of MIL-53(Fe) in the membrane is more favourable in removing higher concentration of MB in water. The capability of the membrane to adsorb more MB in higher concentration of the solution may be attributed to the concentration gradient or driving force inside the solution that pushing more MB molecules to the surface of the membrane (Mahmoodi *et al.*, 2013). The adsorption rate of MB, however, was found slower after 5 hours of contact time. The deficiency of the MB adsorption may be attributed to the insufficient adsorption sites on the surface of membrane as well as lower driving force due to the lower MB concentration (Malik, 2003; Wong & Yu, 1999). Further adsorption experiments on the MIL-53(Fe)/PAN (1:5) by varying the concentration of MB confirmed the ability of the membrane to adsorb more MB at higher concentration of MB solution (see Figure 5).

Adsorption isotherm and Kinetics of MB Adsorption

Figure 5 shows the amount of MB adsorbed by the MIL-53(Fe)/PAN (1:5) membrane with respect to different initial MB concentration, *i.e.* 5, 10, 15, 20, 30, 40 and 60 ppm. The adsorption of MB by MIL-53(Fe)/PAN (1:5) membrane was reaching equilibrium after 8 hours of contact time. The MB adsorptions were analyzed according to the Langmuir (Vijayaraghavan *et al.,* 2006) and Freundlich (Foo & Hameed, 2010) models in order to describe the relationship between the amount of MB adsorbed and its equilibrium concentration in solution. Table 1 shows that the obtained adsorption data is well fitted to the Freundlich model indicating the multilayer coverage of the MB at the surface of the MIL-53(Fe)/PAN membrane. Besides, the value of adsorption intensity, $1/n$ is 1.6 suggesting that the attachment of MB on the surface of MIL-53(Fe)/PAN is governed by cooperative adsorption (Goldberg, 2005; Mohan & Karthikeyan, 1997).

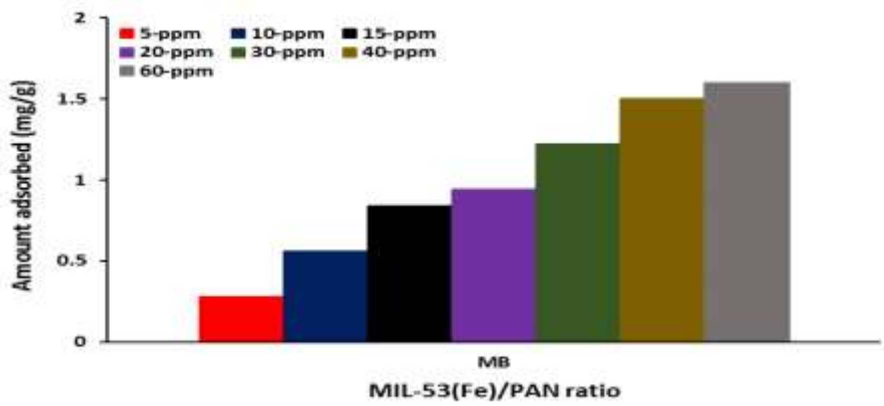

Figure 5. Amount of MB adsorbed by MIL-53(Fe)/PAN (1:5) membrane.

Table 1. Isotherm parameters obtained from Langmuir and Freundlich models.

Adsorbent	Langmuir			Freundlich		
	R^2	q_{max}	K_L	R^2	$1/n$	K_F
MIL-53(Fe)/PAN	0.872	0.860	0.545	0.986	1.586	2.092

The trend of MB adsorption onto the surface of MIL-53(Fe)/PAN membrane was further evaluated by fitting the adsorption data to the *pseudo*-first and *pseudo*-second order kinetics models (Ho, 2006; Ho & McKay 1998). Based on the correlation coefficients, R^2 of the models, it is apparent that the adsorption of MB in water by the MIL-53(Fe)/PAN membrane has good linear relationship with the *pseudo*-first order kinetics model which indicates that the adsorption process was predominated by physisorption (Ho & McKay 1998; Qiu *et al.*, 2009).

Table 2. Correlation coefficients, R^2 of *pseudo*-first and *pseudo*-second order kinetics models with different experiments at initial concentration, C_i of 5-ppm, 10-ppm, 15-ppm, 20-ppm and 30-ppm MB.

Concentration of MB, C_i (ppm)	*Pseudo*-first order		*Pseudo*-second order	
	Correlation coefficients, R^2	Equilibrium rate constant, K_1	Correlation coefficients, R^2	Equilibrium rate constant, K_2
5	0.992	0.00871	0.904	0.00855
10	0.934	0.00852	0.816	0.00559
15	0.909	0.00898	0.526	0.00315
20	0.938	0.00852	0.553	0.00340
30	0.975	0.00813	0.678	0.00774

CONCLUSION

MIL-53(Fe)/PAN membrane has shown good adsorption property over the MB in water. The results showed that, for the fixed amount of membrane, higher amount of MB will be adsorbed at higher concentration of MB in water. This observation can be reasoned by the nature of MB adsorption onto the MIL-53(Fe)/PAN membrane, which is a multi-layered adsorption with physisorption dominating the entire process. This study implies that the prepared MIL-53(Fe)/PAN membrane is capable of removing large amount of pollutants and can be a potential material for air and water purification.

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