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High-performance MOF-based filters for fluoride removal from waste streams

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Abstract—*The production of iron and steel generates large volume of effluent (around 180-200 m^3 of wastewater per ton of steel produced) during cooling, dust suppression, cleaning, heat control, transport of waste, etc. The wastewater contains 150-500 mg/L of fluoride that was introduced (e.g., hydrofluoric acid) during the steel manufacturing process. Fluoride cannot be effectively removed from wastewater using the current common effluent treatment methods. On the other hand, fluoride-containing wastewater from the processing facilities can be recovered at their source. Selective fluoride adsorption from waste streams may be the most effective technology. Metal organic frameworks (MOFs) are a new class of crystalline materials with a high surface area, large pores, and tunable pore channels, making them suitable as adsorbents. This study examines the effectiveness of MOF MIL-96 for fluoride recovery from the effluent of Tata Steel Ltd., Jamshedpur. Wastewater from the blast furnace (170 mg/L) and coke plant (130 mg/L) were collected for this study. The investigation was conducted with synthetic (10-150 mg/L F concentration) and industrial wastewater. MIL-96 reported 90% fluoride recovery at low F concentrations (10-20 mg/L) when using 1 g MIL-96/L of fluoride solution and 98% fluoride recovery at high F concentrations (130-150 mg/L) when using 4 g MIL-96/L of fluoride solution. For industrial wastewater, a similar dose of MIL-96 adsorbent was able to recover 95-97 percent of the fluoride within one hour of the study period at room temperature. Before and after adsorption, the characteristics of the wastewater indicate that phosphate competes with fluoride for the same adsorption sites. MOF MIL-96 was used to produce MOF-filters for industrial scale production. The high fluoride uptake of the MOF filter suggests that these filters could be used in multiple adsorptions-desorption processes.*

1. Introduction

Wastewater discharge from iron and steel, glass making, semiconductor manufacturing, metal smelters, and electroplating industries increases the fluoride concentration in surface and groundwater [1,2]. Various sustainable approaches were used to reduce the fluoride content of industrial wastewater, e.g. electrocoagulation, precipitation and coagulation, ion-exchange, membrane filtration, reverse osmosis, and adsorption [3]. Except for the adsorption process, other approaches are expensive and mainly used for low concentrations of fluoride. The adsorption method was a highly promising technique due to its low operational cost, low energy consumption, simple operation, and robustness [4,5]. Earlier, researchers have reported various adsorbent materials such as activated alumina, calcite, activated coconut shell carbon, activated sawdust, and activated carbon for effective fluoride adsorption [6-11]. According to USEPA and WHO, activated alumina is recognised as the best fluoride adsorbent [12]. It has a large surface area but a low adsorption capacity (2 mg/g). Activated carbon exhibits excellent performance in fluoride removal, under acidic condition, which increases the treatment cost. Industrial wastewater treated with aluminium chloride requires pre-treatment, and treated effluent was unable to reach the standard limit [13]. Therefore, an adsorbent with high water stability, a wide pH range, and high fluoride selectivity is still needed.

Metal-organic frameworks (MOFs) are characterised by a comparatively high void ratio, uniform surface structure, multifunctional groups, and excellent thermal and chemical stability, which make them different from other adsorbents [14,15]. It received more attention due to its adjustable pore size, large surface area, and high adsorption capacity [16,17]. Aluminium fumarate (AlFu) MOF was prepared hydrothermally and has a unique octahedral 3-D crystalline porous structure with a large specific surface area, i.e., 1156 m^2/g. The fluoride uptake capacity of AlFu MOF was much higher (600 mg/g at 25 °C) than that of other MOFs available [18]. The fluoride adsorption capacity of zirconium-based MOF (referred to as MOF-801) was 19.42 mg/g, and it showed the fastest rate of adsorption [19]. Similarly, MIL-96(Al) MOF showed high selectivity towards fluoride ions and high pH stability (3–10). The optimal adsorption capacity was 31.69 mg/g at 25 °C [20]. Most of these MOFs are reported for the low fluoride content of synthetic water.

This study is about the synthesis of MIL-96 MOF (an alkyl-based water-stable MOF). The as-produced MIL-96 MOF was analysed by FESEM, XRD, and a surface area analyzer. The present study investigates the performance of MOF MIL-96 for fluoride recovery from the wastewater of Tata Steel Ltd., Jamshedpur. Wastewater from the blast furnace (170 mg F/L) and coke plant (130 mg F/L) was collected for this study. Important parameters of the adsorption experiment, such as reaction time, adsorbent dose, initial fluoride concentration, and reaction temperature, were

optimised with synthetic fluoride solutions. A MIL-96 MOF filter (filter area = 12.57 cm^2 and MOF content = 0.5 g) was successfully produced and then investigated for industrial wastewater.

2. Materials and methods

2.1 Chemicals

Aluminium nitrate nonahydrate and sodium fluoride were purchased from Merk Life Science Pvt. Ltd. Trimesic acid was purchased from Sigma-Aldrich.

2.2. Synthesis of MIL-96 MOF and filter

MIL-96 MOF was prepared by the hydrothermal method by dissolving Al $(NO_3)_3.9H_2O$ (20.88 g) and H_3BTC (4.09 g) in deionized water (30 ml). The resultant solution was transferred into a 50 mL teflon-lined stainless-steel autoclave (KLB Instruments Co. Pvt. Ltd.) and then heated for 24 hours at 200°C in a hot air oven (i-therm, Mumbai, India). The precipitate was separated by centrifugation at 6000 rpm for 15 minutes and then washed several times with deionized water (REMI R-24, India). Washed MOF was dried at room temperature and then ground with a mortar and pestle into a fine powder. The MOF was further dried for 2 hours at room temperature in a vacuum oven (Stericox, Delhi, India) and then stored in a desiccator.

2.3 Adsorption-desorption study

To investigate the adsorption performance of MIL-96, a batch of experiments was carried out in an orbital shaker (Yorco Sales, Delhi, India) at 120 rpm. For this purpose, a synthetic fluoride solution was prepared in our lab by using the required amount of NaF salt and deionized water. Ideal conditions for maximum fluoride uptake were investigated by varying the (1) adsorption time (10 min-160 min), adsorbent dose (0.3–2 g/L), initial fluoride concentration (5–30 mg/L), and operating temperature (25–55 °C). All the experiments were carried out with a 100-mL synthetic fluoride solution in a 500-mL plastic beaker. The fluoride concentration in the synthetic water was measured before and after the experiment using a fluoride metre (Extech Instruments, FL700, USA). Fluoride removal rate (R%) and adsorption capacity (q_e) of MIL-96 were estimated by eqn. (1) and eqn. (2), where C_O (mg/L) and C_t (mg/L) represent the initial fluoride concentration and the concentration of fluoride at the adsorption time of t in the solution, respectively. q_e (mg/g) is the amount of fluoride uptake per gramme of MIL-96 MOF, V (L) is the volume of working solution, and m (g) is the dosage of MIL-96 MOF.

$$R(\%) = (1 - C_t / C_o) \times 100 \quad (1)$$

$$q_e(mg/g) = (C_o - C_e) \times V / m \quad (2)$$

The adsorption performance of MIL-96 MOF for industrial wastewater was investigated after optimising the experimental conditions with a synthetic fluoride solution. The experiments were conducted with 100 mL of highly concentrated synthetic fluoride solution (150 mg/L) and a different range of adsorbent dose (1–4.5 g/L). The experiments were executed at a natural pH with a reaction temperature of 35 °C. Similar experiments were carried out with industrial wastewater, which was collected in a plastic jerry can from the clarifier tank of a blast furnace and coke plant (TATA Steel, Jamshedpur, India). The initial fluoride concentrations of wastewater from blast furnaces and coke plants are 170 and 130 mg/L, respectively. The adsorption performance of MIL-96 MOF in industrial wastewater was investigated with different adsorbent doses (2–10 g/L). The wastewater characteristics were estimated before and after the adsorption, according to the "standard methods for the examination of water and wastewater" mentioned in the American Public Health Association (APHA et al., 1998). The pH of wastewater was estimated with the help of a pH metre (Lab India, Mumbai, India). The concentration of chloride ions and total hardness of the samples were evaluated by the titration method. The total ammonia of the samples was estimated by a Kjeldahl distillation unit (ACCUMAX, India), and the concentration of phosphate was calculated with the help of a UV-Vis spectrophotometer (Systronics 119, India). The characteristics of the industrial wastewater samples are presented in Table 1.

2.4 MIL-96 MOF filtration study

A MOF filtration study was conducted with wastewater (blast furnace (170 mg/L) and coke plant (130 mg/L)) by using a MIL-96 filter with a radius of 2 cm. The filter was fixed in an empty plastic container with a capacity of 500 mL. Wastewater (a working sample of 300 mL) from the fluoride sample tank was pumped upward and passed slowly through the fixed MOF filter. After the filtration, the filtration time and fluoride concentration of the filtered water were measured, and then the water was transferred back to the fluoride sample tank. This process was repeated up to four times continuously. The schematic representation of this set-up is shown in Figure 1.

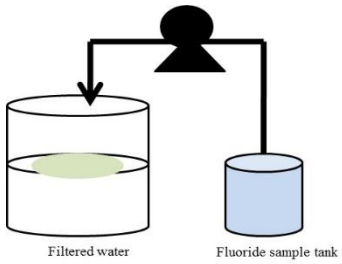


Figure 1: The schematic representation of MOF filtration

2.5 Characterization of MIL-96 MOF

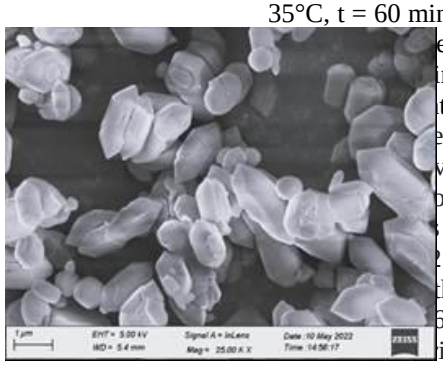
The crystal structure of the synthesised MOF was investigated by the X-ray diffraction technique (XRD) using an X-ray

diffractometer (Rigaku, Japan, Smart Lab 9Kw). To determine the surface area, pore volume, and pore diameter of MIL-96 MOF, Brunauer-Emmett-Teller (BET) analysis was done at 77 K with the help of a surface area analyzer (Quantachrome Instruments, USA). The microstructure of the synthesized MIL-96 MOF was observed by a Field emission scanning microscope (FESEM) (SM-6390LV, Jeol, Japan).

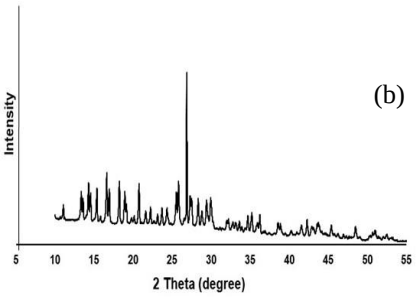
3. Result and discussion

3.1 Characterization of MOFs

The as-produced MIL-96 MOF was analysed by FESEM, XRD, and a surface area analyzer. Figure 2a shows the SEM image of the as-produced MIL-96, which indicates a uniformly distributed pencil-shaped particle with a smooth surface. The XRD pattern of the MIL-96 gives high intensity peaks that look similar (2Θvalues) to $Al_{12}O(OH)_{18}(H_2O)_3(Al_2(OH)_4)$ $(BTC)_6.24H_2O$ as reported earlier [20]. As-prepared MIL-96 MOF was highly crystalline and successfully synthesised by hydrothermal processes (Figure 2b). BET analysis of synthesised MMIL-96 MOF represents its pore volume of 0.07 cm^3/g, pore radius of 0.571 nm, and surface area of 262 m^2/g.



(a)

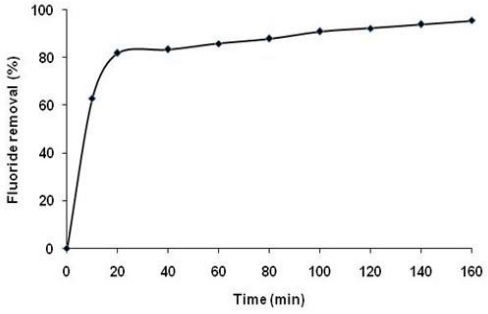


(b)

Figure 2**: (**a)SEM image, and (b) XRD pattern of MIL-96 (Al) MOF.

3.2 Factors influences fluoride uptake capacity of MIL-96 MOF

The effect of reaction time (10–160 min) on fluoride uptake rate was investigated with 1 g/L of MIL-96 MOF, C_o = 10 mg F/L, T = 35 °C, pH = 6 (Figure 3a). More than 82% of fluoride was eliminated in the first 20 minutes of the reaction time, and after that, the process became slower. At the initial stage, the fluoride uptake process was relatively high due to the high intra-particle diffusion of fluoride ions in MIL-96 MOF. After 60 minutes of the reaction, the fluoride concentration reaches the permissible limit for drinking watero = 10 mg F/L, T = 35 °C, pH = 6 (Figure 3a). More than 82% of fluoride was eliminated in the first 20 minutes of the reaction time, and after that, the process became slower. At the initial stage, the fluoride uptake process was relatively high due to the high intra-particle diffusion of fluoride ions in MIL-96 MOF. After 60 minutes of the reaction, the fluoride concentration reaches the permissible limit for drinking water. So, a reaction time of 60 minutes was selected for further experiments. The effect of the MOF dose on fluoride removal and adsorption capacity (q_e) was investigated at different adsorbent doses (0.3–2 g/L) with operating conditions t = 60 min, C_o = 10 mg F/L, T = 35 °C, and pH = 6 (Figure 3b). Fluoride uptake rate increased gradually with an increased dose from 0.3 to 1.2 g/L; after that, no significant removal was achieved. For MOF dose 1.2 g/L, 96% fluoride was removed. The fluoride adsorption capacity (q_e) of MIL-96 MOF decreased with an increased adsorbent dose. The performance of MIL-96 was studied at different ranges of fluoride solutions (5–30 mg/L) with T = 35°C, t = 60 min, MOF dose of 1 g/L, and pH = 6 (Figure 3c). e rate was found to decrease as fluoride ncreased. This happened because, at low trations, the presence of available adsorption er, which will help in the rapid adsorption of vailable adsorbent site and initial fluoride ion of the working solution have become the of this experiment. The effect of reaction 25–55 °C) on fluoride uptake rate was h Co = 10 mg/L, t = 60 min, MOF dose = 1 6. In this investigation, it was found that more ide was adsorbed at all studied temperatures (Figure 3d). Thus, all the experiments were conducted at room temperature.



(a)

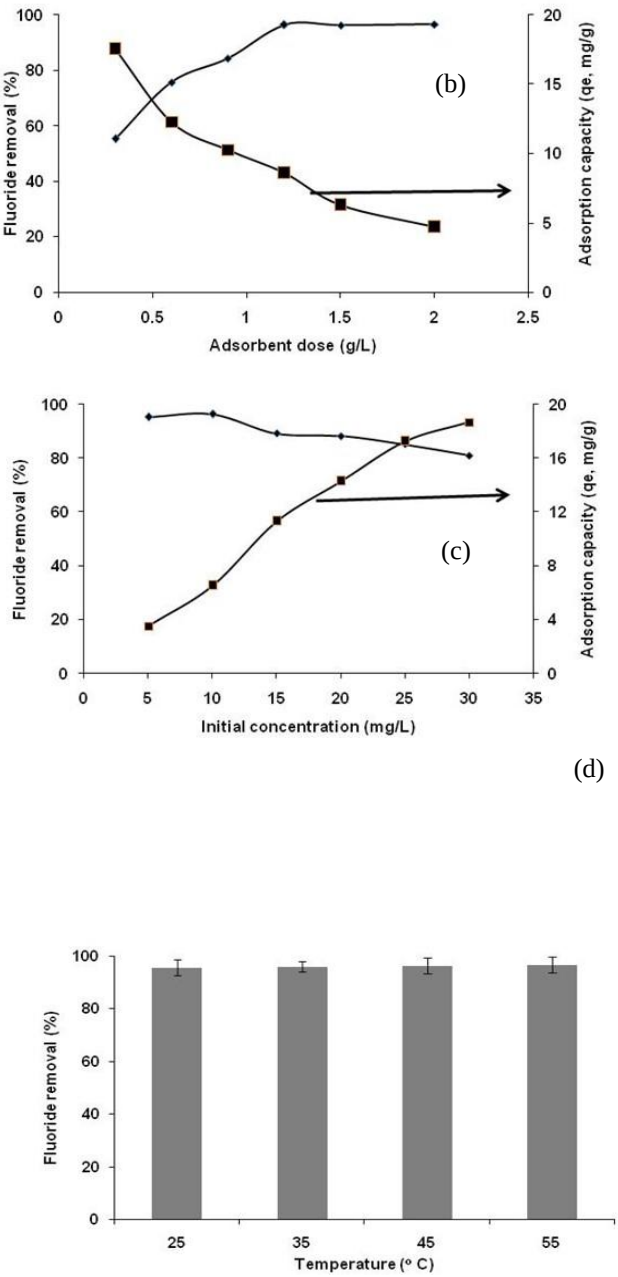


Figure 3: Fluoride adsorption at different (a) reaction time, (b) MOF dose, (c) initial fluoride concentration, and (d) reaction temperature.

3.3 Adsorption study with synthetic and industrial wastewater

To examine the performance of MIL-96 MOF in synthetic wastewater, batch adsorption experiments were carried out with different adsorbent dose ranges from 1 to 4.5 g MOF/L. The reaction was carried out with a high fluoride concentration (150 mg F/L), T = 25°C, t = 60 min, and pH = 6. Figure 4a shows that the fluoride uptake rate of MIL-96 MOF increased with MOF dose. For 2.5 g/L, more than 90% fluoride was absorbed from the synthetic wastewater.

Similar adsorption experiments were conducted in industrial wastewater (blast furnace (170 mg F/L) and coke plant (130 mg F/L)). Fluoride uptake rate was evaluated for adsorbent doses of 2, 3, 4, 6, 8, and 10 g/L. It was observed that 6 g/L of MIL-96 MOF was sufficient for 90% fluoride removal from blast furnace wastewater (Figure 4b), while coke plant wastewater required 4 g/L of MIL-96 MOF for 90% fluoride removal (Figure 4c).

The wastewater characteristics of the blast furnace and coke plant indicate that the concentration of co-existing anions such as total ammonia, chloride, phosphate, and bicarbonates was high. Table 1 represents the different parameters of wastewater from blast furnaces and coke plants before and after the adsorption experiment with MIL-96 MOF. It was noticed that only phosphate ions were reduced in blast furnaces (45%) and coke plants (44%), after the adsorption experiment. This indicates that only phosphate ions compete with fluoride for the active adsorption site.

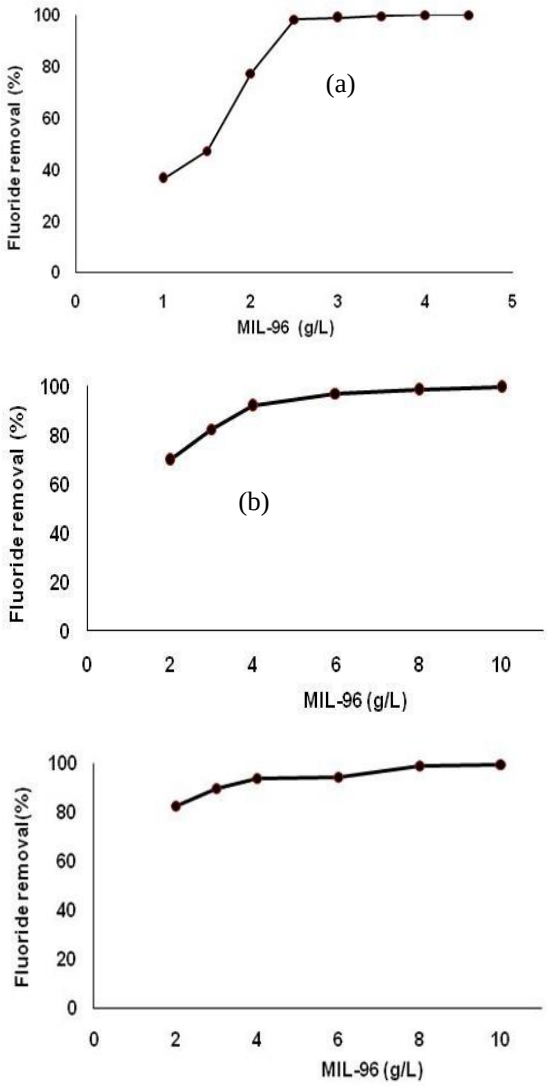


Figure 4: Fluoride uptake rate (%) of MIL-96 MOF at different adsorbent dose in (a)synthetic wastewater, (b) Blast furnace wastewater, and (c) Coke plant wastewater.

Table 1. Characteristic of wastewater (Blast furnace and coke plant) before and after adsorption experiments

Characteristics	Blast furnace (as-received)	Blast furnace (after adsorption)	Coke plant (as-received)	Coke plant (after adsorption)
Fluoride (mg/L)	170±2	1.52±0.2	130±2	0.8±0.1
Chloride (mg/L)	1799±2	1792.4±1	1350±2	1353.6±2
Phosphate (mg/L)	5.85±1	3.21±1	7.45±1	4.16±1
Total ammonia (mg/L)	11.9±2	12.31±2	10.64±1	10.81±2
Total Hardness (mg/L $CaCO_3$)	39.6±2	42±1	59±1	62±2
pH	7.1±0.1	8.4±0.2	7.3±0.2	8.1±0.3

3.4 Performance of MIL-96 MOF filter

The fluoride adsorption performance of the MIL-96 MOF filter was investigated with industrial wastewater (blast furnace and coke plant). Table 2 shows that the MIL-96 MOF filter efficiently reduced 93% of the fluoride ion concentration from the 300 mL wastewater of the blast furnace (170 mg F/L) after 60 minutes of continuous filtration. Similarly, for coke plant wastewater, 90% removal of fluoride was achieved after 35 minutes of continuous filtration (Table 3). This variation was due to the presence of co-existing ions and different initial fluoride concentrations in the blast furnace and coke plant wastewater.

Table 2. Performance of MIL-96 MOF filter in blast furnace wastewater

Cycle	Time (min)	Initial Conc. (mg/L)	Final Conc. (mg/L)
1st	12	170	149
2nd	15	170	133
3rd	16	170	126
4th	17	170	12

Table 3. Performance of MIL-96 MOF filter in coke plant wastewater

Cycle	Time (min)	Initial Conc. (mg/L)	Final Conc. (mg/L)
1st	6	130	86
2nd	8	130	71
3rd	10	130	61
4th	11	130	13

4. Conclusions

This study explores the morphology, porous structure, and fluoride uptake capacity of MIL-96 MOF (Al-based MOF). Batch adsorption experiments reveal that the fluoride uptake capacity is improved with an increase in reaction time and MOF dose in the working solution. 4.5 g/L of MIL-96 MOF was sufficient for complete absorption of fluoride from synthetic water (C_o = 150 mg/L), while wastewater from blast furnaces (C_o = 170 mg/L) and coke plants (C_o = 130 mg/L) needed 10 g/L of MIL-96 MOF. This variation was due to the presence of interfering ions and a different initial fluoride concentration in the working solution. Before and after adsorption, wastewater characteristics show that phosphate ions compete with fluoride ions for the common adsorption sites. The high surface area of MIL-96 MOF (262 m^2/g) resulted in quick fluoride uptake from wastewater. MIL-96 filters effectively participate in the removal of fluoride from blast furnaces (93% after 60 min) and coke plants (90% after 35 min) and are easily scalable for industrial applications.

Acknowledgements

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