



Removal of fluoride from contaminated water by metal organic framework adsorbent – Review

Heeraman Vishwas, Rajat Chatterjee and Chanchal Majumder*

Department of Civil Engineering, Indian Institute of Engineering Science and Technology, Shibpur, Howrah-711 103, West Bengal, India

E-mail: chanchal@civil.iiests.ac.in

Manuscript received online 12 December 2020, accepted 31 December 2020

Defluoridation of contaminated water plays an important part in supply of drinking water to the public within the safe permissible limit. This study emphasizes on summarizing the development and performance of adsorbing materials called metal organic frameworks (MOFs) used in defluoridation studies. For fabrication of MOFs, multivalent metals like Zr, Fe and La are used with crosslinkers like fumaric acid (FA) and chitosan. Characterization of MOFs are done by various techniques like SEM, FTIR, EDAX, etc. MOFs have improved defluoridation capacity, which is affected by several variables like time of contact, sorbent dose, pH, temperature and influence of co-ions etc. The adsorption data is form-fitted with different isotherms. Endothermal-dynamics of the defluoridation process affects its feasibility. Field samples taken and tested with MOFs have been found to diminish the fluoride quantity below the tolerance limit.

Keywords: Defluoridation, MOF composites, contaminated drinking water, organic linker.

Introduction

Fluoride is one of the main toxic elements present in water bodies which can enter in water sources by natural or anthropogenic activity¹. Fluoride is a fundamental micro nutrient for humans in averting dental carries². Depending on dosage of fluoride in water it will cause harmful and beneficial effects on human health. With the rapid development of industrialization, environment pollution is a possible global catastrophe³. Excess consumption of fluoride can lead to adverse health impacts on humans like dental and bone fluorosis⁴. According to WHO, fluoride is thought to be advantageous at a level about 0.7 mg/L but harmful on human well-being if it surpasses 1.5 mg/L⁴. Therefore, removal of fluoride from polluted water is important. Several methods have been developed such as adsorbing media⁵, ion-exchangers⁶, membranes⁷ and electro dialysis⁸. From the above methods, adsorption is chosen due to its ease of operation and lower cost. Some adsorbents used are activated carbon, metal oxides and polymeric materials⁹. These traditional adsorbents have some limitations like poor adsorption capacity, a slim working pH range and bad mechanical sturdiness¹⁰.

Metal organic framework (MOF) synthesized by using metal ions in conjunction with organic ligands (crosslinkers)

have been expansively explored as structured high porosity sorbents^{11,12}. The greatest advantage of nanomaterial MOF with respect to traditional adsorbents is that their pore size and sorption surface area can be finetuned by selectivity of diverse metallic ion-organic-ligand combination¹³.

If adsorbents with more practical applicability in de-fluoridation of water are to be made, sorbents based on nanomaterials have to be utilized¹⁵. Nanomaterial based adsorbents are widely used owing to their great affinity towards fluoride contaminants¹⁴. Nanomaterials of graphene oxide have been used to provide an organic mesh for the interaction of metal ion with the crosslinker¹⁶. Zirconium based anion exchange resins impregnated into a graphene oxide (GO) nanoparticle mesh were used for scavenging of fluoride from water. It saw fast fluoride exchange rates, with a whopping equilibrium period of 5 min¹⁷. A Zr(IV)-chitosan (CS) MOF membrane showed fluoride sorption capacity of 48.26 mg/g¹⁸. In another study, Zr-CS/GO hybrid membrane was able to achieve defluoridation by exchanging ions as a result of Zr-F formation. This MOF was seen to have a wide active pH range and a sorption of 29 mg/g¹⁹.

In 2010, researchers stated the use of MIL101 (Material Institute Lavoisier) for the elimination of organic dyes²⁰. Very

recently, the application of MIL96 was first reported for fluoride scavenging²⁰. Regrettably, Al based MOFs are unsafe due to the enduring Al ions even after treatment. There are some non-toxic iron-based MOFs (MIL53, MIL88A and MIL100) that have shown promise. MIL88A is a three dimensional porous system of oxo-centered trimers of Fe octahedra inter-connected using FA ligands²¹.

Synthesis of MOFs

MOFs are prepared by the use of a multivalent metal and an organic polymer linker. In this section, synthesis procedures for MOF-based adsorbents have been discussed along with the materials required in the process. Specific focus was given to MOFs used in the removal of F⁻ from polluted water.

Zirconium MOF:

Zirconium as metal Zr⁴⁺ and FA as organic polymer were chosen for the synthesis of this MOF. Zr⁴⁺ was selected because it is easily available, cost-effective and has satisfactory removal efficiency. The advantage of fumarate-based MOF are truncated costs and relaxed operation^{22–24}. Zirconium oxychloride (ZrOCl₂) and the organic polymer FA was used as N, N-dimethyl formamide (DMF). Ethyl alcohol, NaCl, NaNO₃, Na₂SO₄, NaF and acetone were bought from suitable sources. Zirconium fumarate (Zr@Fu) was prepared by the hydrothermal technique^{25,26}. Zr-oxychloride and FA were liquefied in DMF at STP. The subsequent solution was transported to a Teflon coated autoclave and heated for 1 day. The product was then washed and oven dried.

Iron MOF:

Fe based MOFs, chiefly that based on iron coordinated with FA (MIL88A) have been utilized for defluoridation. Material used are FA (HO₂C-C₂H₂-CO₂H) and FeCl₃.6H₂O. The fluoride ion stock (1000 ppm) was made with NaF in DI water. The iron-based MOFs such as MIL53, MIL100 and MIL101 were arranged following the stated technique^{27–32}. Here, FeCl₃.6H₂O and FA were dissolved in DI water. The mixture was stimulated gradually and then transferred into an autoclave for heating. After refrigeration to STP, the attained product was purified composed by centrifugation, washed and finally dried overnight at 120°C.

Aluminum MOF:

Aluminum MOF was also formed by hydrothermal analy-

sis³². For making aluminum fumarate materials used are alum Al₂(SO₄)₃.18H₂O, fumaric acid and sodium hydroxide, NaOH. Equipment used here are glass reactor.

MOF was prepared by adding these chemicals in suitable amount in the deionized water and heated. Another solution is prepared by adding fumaric acid and NaOH in water. After heating, a white coloured precipitate of aluminum fumarate was obtained and isolated by the action of centrifugation. Some untreated reagents are present which are washed several times by using water.

Lanthanum MOF:

Materials used for making this MOF are benzene-1,4-dicarboxylic acid (BDC), LaCl₃, NaF, Na₂SO₄, DMF, NaHCO₃, NaCl and NaNO₃. Lanthanum MOF was molded by hydrothermal method^{33,34}. LaCl₃.7H₂O and BDC, 2 mmol each are completely dissolved in DMF at ambient temperature. A similar procedure to the MOFs mentioned earlier was followed in synthesis.

Cesium MOF:

Ce ion implanted MOF (MIL96) was made with 1,3,5-benzentricarboxylic acid (H₃BTC), Ce(NO₃)₃ and Al(NO₃)₃. A similar procedure to the MOFs mentioned earlier was followed in synthesis³⁵.

Characterization studies

Zirconium MOF:

Functional groups present in Zr@Fu MOF are studied by FTIR spectroscopy. FTIR functions on certain range of wavelength. There are some fixed wavelengths where MOF composites showed sharp peaks.

It confirmed the immediacy of carboxyl and carbonyl groups between 1400 and 50 cm⁻¹. A sharp band peak at 1656 cm⁻¹ in fluoride adsorbed Zr@Fu was attributed to the electrostatic attraction amid the fluoride and the MOF Zr@Fu. Wavenumber 3452 cm⁻¹ in Zr@Fu designated that the hydroxyl OH⁻ ion groups had been merged into the composite. In some instances, the peaks in virgin MOF reduced due to substitutable hydroxyl ions displaced by F⁻ in the loaded MOF^{22–24}.

Iron MOF:

The crystal structure and surface morphology of the synthesized sample were studied by X-ray diffraction (XRD) and scanning electron microscope (SEM) analysis. The XRD

Table 1. Optimum values of parameter which affect the fluoride adsorption

Sl. No.	MOF	pH	Adsorbent dose (g)	Temp. (K)	Contact time (min)	Concentration fluoride (mg/L)	Adsorption capacity (mg/g)	Ref.
1.	Zr	5	0.05–0.25	303	30	10	4.920	25, 26
2.	Fe	6	0.6964	298	10	10	40.42	27, 32
3.	Al	7	1.5	293	20	30	600	32
4.	La	–	–	298	–	3.68	4.9	33, 34
5.	Ce	6	0.59	298	20	10	38.65	35

analysis clearly confirmed that the synthesized product was crystalline solid in nature^{27–32}. No diffraction peaks of impurity were seen, representing the formation of MIL88A. The obtained MIL88A product looked like thin projections with slight size distribution in SEM.

Aluminum MOF:

Gold coated samples were studied by SEM. Surface area and pore diameter for Al@Fu were attained from Brunauer-Emmett-Teller examination at 77 K. The changes in physical-chemical properties of the Al@Fu were found by thermogravimetric analysis³².

Lanthanum MOF:

FTIR spectra of La@BDC pre and post adsorption were portrayed. In La@BDC, 1400–1700 cm^{-1} designated the characteristic vibrational frequencies of groups: carboxyl or carbonyl. XRD analysis was used for determination of crystalline nature of La@BDC. SEM of the La@BDC pre and post fluoride adsorption were inspected^{33,34}.

Experimental studies

Batch studies:

The defluoridation experiments were performed in batch method to find out the effect of different parameters which affect behavior of pollutants present in contaminated water. Here we establish the relation between adsorbent and parameter present in water which affect the adsorption capacity of adsorbent³⁴.

Parameters affecting MOF efficiency:

Effect of contact time was studied to determine the equilibrium contact time for maximum F^- sorption. It was shown that Zr-MOF composites got to equilibrium at a minimum contact period of 30 min^{22–24}.

pH is an important variable interfering with defluoridation. The adsorption of F^- onto MOF was carried out at different

pH levels and by keeping remaining parameters stable. Highest defluoridation capacity was seen at low pH, and lower most at high pH²².

Effect of adsorbent dose is also one of the significant parameters affecting adsorption. MOF active sites increase with dosage, which helps to adsorb greater number of fluoride ions^{16,36,37}. Initially, the adsorption was quick (up to certain limit of removal of fluoride ion). Further adsorbent addition created no effective active sites. Equilibrium batch study parameters from different case studies have been mentioned in Table 1.

Effect of co-existing ions:

In general, polluted waters always contain some co-existing ions along with F^- , which may contest with F^- for active adsorption sites³². Co-existing anions which were present in the contaminated water were Cl^- , NO_3^- , CO_3^{2-} and SO_4^{2-} . Concentrations of Cl^- , NO_3^- and SO_4^{2-} were found to be less significant compared to CO_3^{2-} . Adsorption capacity decreased as the concentration of CO_3^{2-} increased. Effect of co-existing ions was measured while preserving all other parameters constant at STP.

Statistical tools:

Subsequently plotting sorption isotherms from equilibrium information, statistical tools were used to regulate goodness of fit. The goodness of fit of each model was deliberated using standard statistical methods like χ^2 -analysis. Regression coefficient (R^2) and deviation were designed accordingly to confirm the most appropriate isotherm model for fluoride sorption studies³⁸.

Conclusion

MOFs are synthesized using a multivalent metal ion and an organic crosslinker. Metals like Zr, Fe and La are used while crosslinkers like FA and chitosan are utilized. Nanomaterials of graphene oxide have also been used to

provide an organic mesh for the interaction of metal ion with the crosslinker. The MOF composites show defluoridation capacities as high as 4920 mg F⁻/kg. The defluoridation capacity is affected by pH and the presence of carbonate groups. The sorption of fluoride on MOFs usually follows the Langmuir isotherm, with the nature of the reaction being spontaneous and endothermic. The fluoride-MOF interaction at microscopic level is generally because of electrostatic pull and ionic competition. The outcomes of field studies validate that MOF composites could be used as hopeful de-fluoridating ingredients for safe water supply.

References

- B. Walna, I. Kurzyca, E. Bednorz and L. Kolendowicz, *Environ. Monit. Assess.*, 2013, **185(7)**, 5497. doi: 10.1007/s10661-012-2962-9.
- W. Y. Fantong *et al.*, *Environ. Geochem. Health*, 2010, **32(2)**, 147. doi: 10.1007/s10653-009-9271-4.
- H. Tong, S. Ouyang, Y. Bi, N. Umezawa, M. Oshikiri and J. Ye, *Adv. Mater.*, 2012, **24(2)**, 229. doi: https://doi.org/10.1002/adma.201102752.
- L. H. Velazquez-Jimenez, R. H. Hurt, J. Matos and J. R. Rangel-Mendez, *Environ. Sci. Technol.*, 2014, **48(2)**, 1166. doi: 10.1021/es403929b.
- A. Dhillon, M. Nair, S. K. Bhargava and D. Kumar, *J. Coll. Int. Sci.*, 2015, **457**, pp. 289. doi: 10.1016/j.jcis.2015.06.045.
- X. S. Yi *et al.*, *Desalination*, 2012, **286**, 254. doi: 10.1016/j.desal.2011.11.032.
- S. Chakraborty, M. Roy and P. Pal, *Desalination*, 2013, **313**, 115. doi: 10.1016/j.desal.2012.12.021.
- M. Bhaumik, T. Y. Leswif, A. Maity, V. V. Srinivasu and M. S. Onyango, *J. Hazard. Mater.*, 2011, **186(1)**, 150. doi: 10.1016/j.jhazmat.2010.10.098.
- K. S. Prasad, Y. Amin and K. Selvaraj, *J. Hazard. Mater.*, 2014, **276**, 232. doi: 10.1016/j.jhazmat.2014.05.038.
- L. Chai, Y. Wang, N. Zhao, W. Yang and X. You, *Water Res.*, 2013, **47(12)**, 4040. doi: 10.1016/j.watres.2013.02.057.
- H.-C. Zhou, J. R. Long and O. M. Yaghi, "Introduction to metal-organic frameworks", ACS Publications, 2012.
- Q.-L. Zhu and Q. Xu, *Chem. Soc. Rev.*, 2014, **43(16)**, 5468. doi: 10.1039/C3CS60472A.
- S. S. Nagarkar, B. Joarder, A. K. Chaudhari, S. Mukherjee and S. K. Ghosh, *Angew. Chem.*, 2013, **125(10)**, 2953. doi: https://doi.org/10.1002/ange.201208885.
- P. Silva, S. M. F. Vilela, J. P. C. Tomé and F. A. A. Paz, *Chem. Soc. Rev.*, 2015, **44(19)**, 6774. doi: 10.1039/C5CS00307E.
- M. C. Das *et al.*, *J. Am. Chem. Soc.*, 2012, **134(20)**, 8703. doi: 10.1021/ja302380x.
- R. Chatterjee and C. Majumder, *Journal of Water Process Engineering*, 2021, **39**, 101686. doi: 10.1016/j.jwpe.2020.101686.
- J. Zhang *et al.*, *Langmuir*, 2019, **35(21)**, 6861. doi: 10.1021/acs.langmuir.9b00589.
- Q. Liu, L. Zhang, B. Yang and R. Huang, *Int. J. Biol. Macromole.*, 2015, **77**, 15. doi: 10.1016/j.ijbiomac.2015.03.008.
- J. Zhang, N. Chen, P. Su, M. Li and C. Feng, *React. Funct. Polym.*, 2017, **114**, 127. doi: 10.1016/j.reactfunctpolym.2017.03.008.
- N. Zhang *et al.*, *Chem. Eng. J.*, 2014, **252**, 220. doi: 10.1016/j.cej.2014.04.090.
- H. Furukawa *et al.*, *J. Am. Chem. Soc.*, 2014, **136(11)**, 4369. doi: 10.1021/ja500330a.
- F. Keet *et al.*, *Scientific Reports*, 2018, **8(1)**, Art. no. 1. doi: 10.1038/s41598-018-19277-2.
- S. Karmakar, J. Dechnik, C. Janiak and S. De, *J. Hazard. Mater.*, 2016, **303**, 10. doi: 10.1016/j.jhazmat.2015.10.030.
- S. Karmakar, S. Bhattacharjee and S. De, *J. Environ. Chem. Eng.*, 2017, **5(6)**, 6087. Dec. doi: 10.1016/j.jece.2017.11.035.
- M. Hasanzadeh, A. Simchi and H. S. Far, *Mater. Chem. Phys.*, 2019, **233**, 267. doi: 10.1016/j.matchemphys.2019.05.050.
- P. Horcajada *et al.*, *J. Am. Chem. Soc.*, 2008, **130(21)**, 6774. doi: 10.1021/ja710973k.
- J. W. Yoon *et al.*, *Angew. Chem. Int. Ed.*, 2010, **49(34)**, 5949. doi: https://doi.org/10.1002/anie.201001230.
- S. Bauer *et al.*, *Inorg. Chem.*, 2008, **47(17)**, 7568. doi: 10.1021/ic800538r.
- P. Horcajada *et al.*, *Nature Materials*, 2010, **9(2)**, Art. no. 2. doi: 10.1038/nmat2608.
- C. Kiener, U. Muller and M. Schubert, "Organometallic aluminum fumarate backbone material", US20090092818A1, April 09, 2009.
- E. Leung, U. Müller, N. Trukhan, H. Mattenheimer, G. Cox and S. Blei, "Process for preparing porous metal-organic frameworks based on aluminum fumarate", US8524932B2, September 03, 2013.
- A. Jeyaseelan, Mu. Naushad and N. Viswanathan, *J. Chem. Eng. Data*, 2020, **65(6)**, 2990. doi: 10.1021/acs.jced.0c00005.
- K. Pandi and N. Viswanathan, *Carbohydr. Polym.*, 2015, **118**, 242. doi: 10.1016/j.carbpol.2014.10.068.
- C. Mellot-Draznieks, C. Serre, S. Surblé, N. Audebrand and G. Férey, *J. Am. Chem. Soc.*, 2005, **127(46)**, 16273. doi: 10.1021/ja054900x.
- X. Yang, S. Deng, F. Peng and T. Luo, *Dalton Trans.*, 2017, **46(6)**, 1996. doi: 10.1039/C6DT03934K.
- R. Chatterjee and C. Majumder, *J. Indian Chem. Soc.*, 2020, **97(4)**, 501. doi: https://indianchemicalsociety.com/

- journal/abstract_details.php?journal=MzI1.
37. R. Chatterjee and C. Majumder, *J. Indian Chem. Soc.*, 2019, **96(4)**, 499. doi: https://indianchemicalsociety.com/journal/abstract_details.php?journal=MzU.
38. S. Chaudhuri, R. Chatterjee, S. K. Ray and C. Majumder, *J. Indian Chem. Soc.*, 2020, **97(4)**, 541. doi: https://indianchemicalsociety.com/journal/abstract_details.php?journal=MzMx.