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Short Communication

Zn Based Metal Organic Framework as Adsorbent Material for Mecoprop

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Abstract

Metal organic framework, a new class of hybrid materials is now involved in a number of applications based on size and distribution pattern of its pores. Present research focus on Mecoprop adsorbent capacity of Basolite, a zinc based metal organic framework. Basolite ($C_8H_{12}N_4Zn$) having a pore width 11.6Å and pore aperture 3.4Å has been used here for entrapping Mecoprop a commonly used pesticide which has very high mobility and a common contaminant for aquatic systems. Due to a very high surface area i.e 1300-1800 m^2/gm of basolite and specific pore size it is found to be very efficient for adsorption purpose and another important property of Basolite is that it gets reactivated at 100^{o}C so can be used again and again. Adsorption of pesticide by Basolite column was confirmed by UV Visible spectroscopy. The study revealed that Basolite adsorb Mecoprop due to entrapment of Mecoprop inside its pores. Basolite can be used for preparing filters on large scale for removing harmful pesticide from aquatic systems.

Keywords: Metal organic frameworks, mecoprop, environment, water quality, filter

Introduction

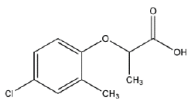
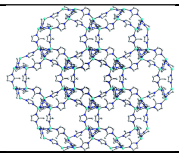
Environmental pollution by organic chemicals continues to be one of the most alarming challenges to sustainable development. Pesticides persist in the environment for long times due to their long half lives[1,2]. Adsorption has always been the choice of treatment in case of polluted water[3,4]. It is not long back when zeolites and activated carbon[5] known to be more versatile adsorbents for pollutants. But as the need grows for more efficient, economical, specific adsorbents, conventional adsorbents were not found effective enough to deal with such problems. Synthesizing and using novel and smart materials has long been cherished as a stepping stone in technological advancement. Metal Organic Frameworks are a special class of organic Coordination Polymers (CP) which are crystalline and porous compounds having strong metal ligand interactions and generally belongs to the second and third generation of CPs whose crystal structure is made up of extended 3 D network of small discrete clusters/ small ions connected by multi dentate organic linkers. Compared to other types of metal organic framework materials, Zeolitic Imidazole Framework (ZIF) often showed better thermal, hydrothermal and chemical stabilities[6,7]. Basolite (ZIF 8) has well known applications in separation, gas storage, chemical sensor[8], catalysis but no work has done so far on the pesticide absorbing capabilities of it on the basis of its pore size[9]. Due to this ZIF 8 can be used for making filters for removing pesticide from a given sample. In the present work ZIF 8 has been used as adsorbent material for Mecoprop or methylchlorophenoxypropionic acid (MCPP), commonly used man-made herbicide used as a weed killer and "weed-and-feed" kind of lawn fertilizers. It is commonly used for controlling broadleaf weeds. Mecoprop is an odorless, white to light brown crystalline solid that dissolves very easily in water and is also soluble in some organic solvents. Due to its low affinity for soil and high mobility it easily leaches to ground water. Half life is from one to several weeks but in crystalline form it may even persist for much longer time period[10]. Several studies have showed that there is no abiotic degradation of Mecoprop. MCPP was found to be most frequently detected herbicide in both urban and rural environment in U.K [11] and 6th most sold herbicide in Denmark (1959-2005). Mecoprop is also present in plan of work of rolling revision of the WHO Guidelines for drinking water quality[12]. Mecoprop has a low toxicity to birds and to fish but it is recommended not to contaminate water as a general precaution. Excessive exposure to Mecoprop may affect the digestive system, reproductive system, eye, skin and even carcinogenic[13,14].

Material and Methods

Basolite Z1200 ($C_8H_{12}N_4Zn$) by Sigma-Aldrich and Mecoprop (IUPAC name -2-(4-chloro-2-methylphenoxy) propanoic acid) by Fluka Analytical was used without any further modification. Details of material are given in table-1. The white colored MOF powder was firstly activated at 100^{0}C.

Filter preparation: 200 mg activated ZIF-8 was dissolved in 5 mL ethanol and then sonicated for 15 minutes to obtain homogeneous suspension. A micro centrifuge filter was used for column formation, which was previously washed with ethanol to remove any impurity. 100 µl of ZIF-8 suspension was poured into the micro centrifuge filter. It was allowed to settle for 15 minutes until most of the ethanol filtered through. These steps were repeated for the whole solution. It was then allowed to settle completely for 20 minutes.

Table-1
Showing properties of Mecoprop and Basolite Z1200[15,16]

Chemical name: Mecoprop/ methylchlorophenoxypropionic acid . (MCPP)	Chemical structure: 	Chemical formula: $C_{10}H_{11}ClO_3$	pKa 3.78	Kd 0.07
Basolite Z1200 Zeolitic Imidazole Frameworks/ 2-methytlimidazolezinc		$C_8H_{12}N_4Zn$	Reactivation Temperature 100°C	Bulk density 0.35g/cm^3

Pesticide Filtration: Herbicide stock solution of concentration 1mg/ml was prepared in ethanol; it was introduced in the prepared column in small lots of 100 µL with the help of a micropipette. A number of mecoprop aliquots were injected in the column as elaborated above and concentration of the analyte in the collected filtrates was recorded on UV-Visible spectrophotometer in the range between 240-550 nm.

Absorption studies were confirmed by UV-Visible spectrophotometer in the range between 240-550 nm.

Results and Discussion

The absorption spectrum of Mecoprop was recorded and was obtained at 280 nm which was further confirmed by literature[17]. Calibration curve for Mecoprop is drawn for further quantitative studies as shown in figure-1.

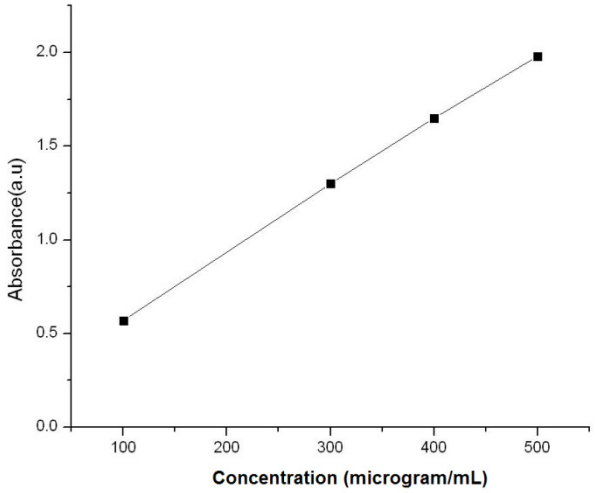


Figure-1
Showing calibration curve for Mecoprop

Stock solution shows λ_{max} at 280 nm. When 100 µl stock solutions was allowed to passed through the filter made up of MOF and filtrate is checked for pesticide conc. the intensity of absorption peak decreases significantly confirming that ZIF 8 has absorbed pesticide from the stock solution.

It can be seen from calibration curve and absorption graph that as compared to the initial concentration of pesticide stock i.e. 1mg/ml the concentration of Mecoprop decrease significantly as low as 50 µg/ml as seen in figure-2. Up to 7 aliquot additions the concentration was lower than 200 µg/ml. After that it starts increasing due to saturation of Basolite filter. Thus, the percentage decrease in concentration is approximately 80%. The high adsorption by Basolite is due to its very high surface area as compared to activated carbon (1 gm industrially produced activated carbon have surface area of 400-1500 m^2 [18] whereas basolite has a very high surface area i..e 1300-1800 m^2/gm) . Basolite has pore width 11.6Å and pore aperture 3.4Å and due to comparable dimensions of mecoprop i.e. length 9.43 Å and width 4.88Å [19] mecoprop get entrapped.

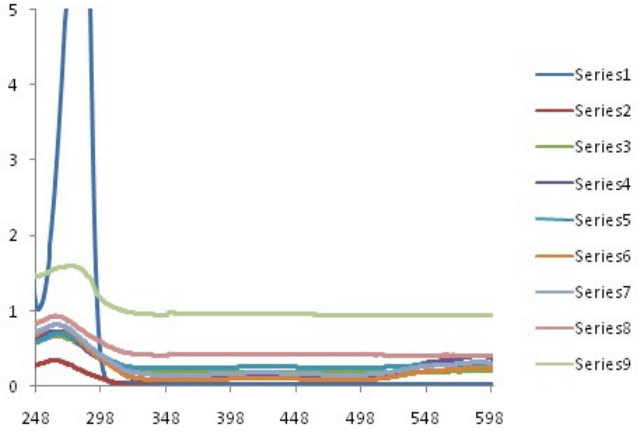


Figure-2
Showing Absorption spectra of Mecoprop stock and series of filtrate obtained after passing stock through Basolite filter

Basolite get reactivated at 100^{0}C and can be reused. Figure-3 shows the absorption of mecoprop by basolite filter after its reactivation.

Conclusion

Basolite is found to be very efficient to adsorb pesticide Mecoprop up to a significant amount. Filter can thus be produced on large scale for removing Mecoprop from drinking

water. Reactivation property of Basolite make it more economical and can be used for long term treatment systems.

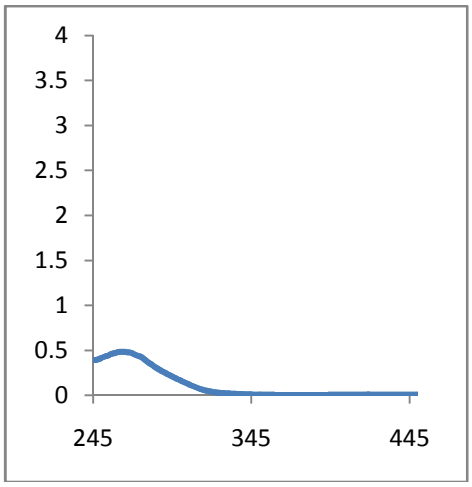


Figure-3
Showing Absorption spectra of Mecoprop stock after reactivation of filter

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