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Iron Removal from Drinking Water System using Ecofriendly Synthesized Metal-Organic Frameworks

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ABSTRACT

Urbanization and industrialization had decreased the drinking water quality to a greater extent. Iron contamination is a serious issue in many open well and bore well samples of Kerala, India. Intake of large amount of iron causes serious health issues to humans. There were several methods for the removal of iron from drinking water. But the cost of these treatments is not affordable to common people. Use of eco-friendly materials for the effective removal of iron from water samples is the major concern for this study. Different plant materials which are easily available in Kerala were used in this study for the effective removal of iron. Clitoria ternatea, which is a climber was selected as the adsorbent material. The extracts of this plant materials were incorporated in Magnesium based Metal-Organic-Framework (MOF) and used for water treatment. Among the prepared MOFs, that modified with flower extract of Clitoria ternatea, was found to be more effective at an adsorbent dosage of 40ppm. The adsorption process was analyzed using different isotherms and found suitable for Langmuir adsorption. Hence a mono-layer of adsorption was formed on the adsorbent surface by physical adsorption.

Keywords: Metal-Organic Framework, Adsorption, Clitoria ternatea, Langmuir adsorption isotherm

INTRODUCTION

Ground water is the major source of drinking water and its quality is greatly affected by both natural and man-made causes. Maintenance of drinking water quality standards is very difficult nowadays due to urbanization and industrialization[1]. Studies showed that some drinking water quality parameters were exceeding the limit in the samples collected from many open and bore wells of Kerala, India[2]. Iron is the major contaminant in these samples[3]. Increased amount of iron in water will increase the bacterial growth and will produce an unpleasant odour. It also affects household fittings and even human health. Excessive intake of iron in the body may leads to cardiovascular diseases, Parkinson's, diabetes mellitus, Alzheimer's, hyperkeratosis, like chronic cholic infection, diarrhoea, cholera[1,4] etc. It also affects the immunity of human beings too. In water, iron is present in two different forms, one is in ferrous iron and the other one is ferric iron. Ferrous iron may dissolve in water and does not affect the color of the water. But it gives a metallic taste to water. On oxidation, ferrous iron changes to ferric iron results in yellow-brown precipitate, which gives water a yellowish brown colour. It was reported by World Health Organisation (WHO) that the amount of iron found in drinking water should be less than 0.3 ppm.

There are several methods for the removal of excess iron from water. These include hydrogenation[5], oxidation[6-8], bio-remediation[9] etc. Bio-remediation is less harmful to the environment, but its effectiveness decreases as pollution increases. Different materials were synthesized for the removal of iron by altering their physio-chemical properties. Adsorption is the best method which is highly efficient technique and has low cost of operation. Many naturally occurring materials can be used as adsorbent. The selective adsorption of pollutants from water samples by the adsorbent is also a very important factor to determine the efficiency of this process. Despite of these advantageous, adsorption has disadvantage such as disposal problem and reliability for real application in water samples.

Metal-organic frameworks (MOFs) have received important attraction in adsorption field, owing to specific constructive characteristics that are not found in other poriferous materials. The elastic and exceedingly porous structures of MOFs make the diffusion of the guest ions or molecules easy into the bulk structure[10]. The presence of biosorbents have good adsorption capacity for iron removal from water sample. Since biosorbents contain groups like amine, amide, sulfonate, carbonyl and phenolic functional groups that can attract metal ions easily[11]. To increase the effectiveness, the microorganism must be immobilized on suitable surface[12]. Natural extracts prepared from different parts of plants like seeds, leaves, bark or sap, roots, and fruits were used for water treatment from ancient times[13-15].

Aim of the study is to synthesize a material which has the properties of low cost, ease of availability in more amount and simple desorption of the adsorbed metal ion and reproducibility of the material. So, a low cost magnesium metal was selected for the synthesis of MOF and the flower and leaf extracts of Clitoria ternatea (which is otherwise called butterfly pea plant) as the biosorbent for its modification. Clitoria ternatea is an attractive climber, grows up to 2–3 m tall, bears blue or white flowers which is locally available in the southern part of Kerala. The extract of Clitoria ternatea leaves were used as reducing agents to synthesize various nano particles[16,17].

MATERIALS AND METHODS

Preparation of plant extract incorporated Mg-MOF

Mg-MOF nano particles were synthesized by incorporating the flower extract of Clitoria ternatea as in the previous part of this study[18]. The synthesis was carried out using a microwave oven of Samsung MS2 3F301E made. The leaf extract incorporated Mg-MOF was prepared from the leaves of Clitoria ternatea by using the same procedure.

Adsorption studies

The water samples were collected from borewell near Sanghumugham, the Coastal area of Thiruvananthapuram, Kerala. It was filtered using Whatman No. 40 filter paper to remove macro contaminants and initial iron concentration was estimated using a spectro-photometer at a wavelength of 565nm[19]. The iron removal efficiency was studied by adding 2, 4, 10, 20, 40 ppm each of pure Mg-MOF, flower extract incorporated Mg-MOF and leaf extract incorporated Mg-MOF. All these samples were shaken well and kept without any disturbance. The absorbance value of each sample is measured after definite interval of time and suitability of different isotherms were also analyzed.

RESULT AND DISCUSSION

Physio-chemical characteristics of borewell water

The physio-chemical characteristics were measured for borewell water sample and are given in Table 1.

Table 1: Characteristics of borewell water

Sl. No	Parameters	Values
1	Turbidity	48
2	pH	7.2
3	Conductivity (µScm^{-1})	1312
4	Dissolved Oxygen (mg/L)	8.2
5	Chloride (mg/L)	200
6	Alkalinity (mg/L)	234
7	Calcium Hardness (mg/L)	174
8	Mg Hardness (mg/L)	120
9	Total Hardness (mg/L)	302
10	Total Solids (mg/L)	945
11	Total Dissolved Solids (mg/L)	839
12	Total Suspended Solids (mg/L)	99

Determination of initial iron concentration of bore well water

Initial iron concentration of collected bore well water sample is determined by using freshly prepared ferrous ammonium sulphate as the standard in spectrophotometer at 565nm. A calibration curve was drawn using ferrous ammonium sulphate(1000 ppm) with different concentration of 2, 4, 6 and 8 ppm. After that unknown concentration of iron in borewell water sample was determined. Absorbance vs concentration was plotted and the Y-intercept was obtained slope and correlation were measured for each sample at 565nm which is shown in Figure1.

The ferrous ion concentration in borewell water sample was 0.4401 ppm from this graph. According to the Indian Standard Drinking Water-Specification value IS: 3025 (Part 53), the normal water should contain the ferrous ion less than 0.3 ppm 20.

Effect of adsorbent dosage

The iron removal efficiency of each adsorbent was studied by adding 2, 4, 10, 20, 40 ppm each of pure Mg-MOF, flower extract modified Mg-MOF and leaf extract modified Mg-MOF. Effect of adsorbent dosage on iron removal is shown in Figure 2.

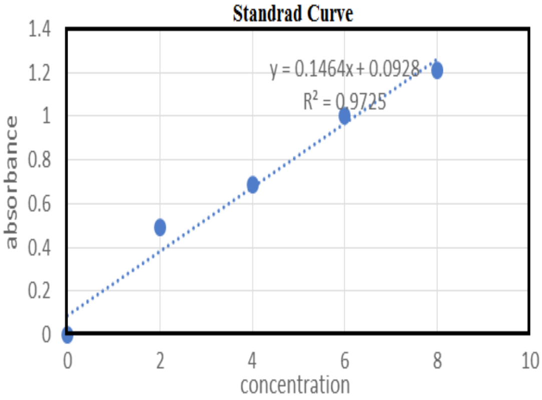

Fig. 1. Calibration of ferrous ion using spectrophotometer at 565nm

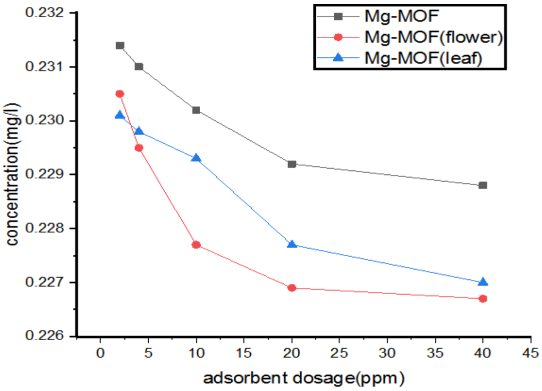

Fig. 2. Effect of adsorbent dosage of the prepared MOFs

From the figure it is clear that, as the concentration of the adsorbent increases, more and more iron is removed from the water samples. This is mainly due to increase in the surface area of the adsorbent. All the three prepared MOFs were found to be effective in iron removal. But after 40 ppm of adsorbent dosage, the iron concentration in water samples remain almost constant which means most of the adsorbent surface get occupied by the adsorbate. Hence, maximum effectiveness is observed in 40 ppm of the adsorbent dosage. Among the prepared MOFs, that prepared from the flower extract of Clitoria ternatea was found to be most effective in iron removal from water sample.

Study of adsorption and iron removal efficiency

The adsorption efficiency and iron removal efficiency with respect to adsorbent dose was studied for all the three prepared samples using the equations.

Adsorption efficiency (%) = $[(C_i - C_e) \times 100]/C_e$

Removal efficiency (%) = $[(C_i - C_e) \times 100]/C_i$

Where C_i and C_e are initial and final concentrations of iron in water sample. These are shown in Figures 3(a), 3(b) and 3(c).

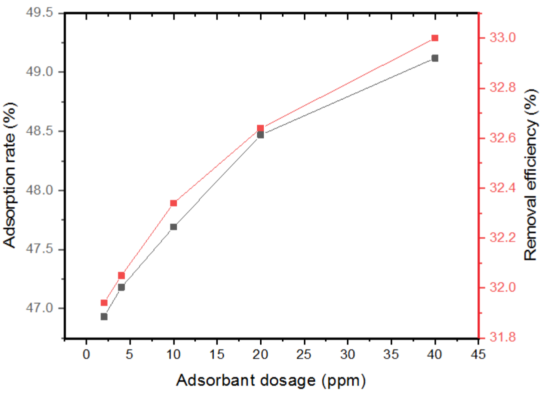

Fig. 3a. Adsorption and iron removal efficiency of pure Mg-MOF

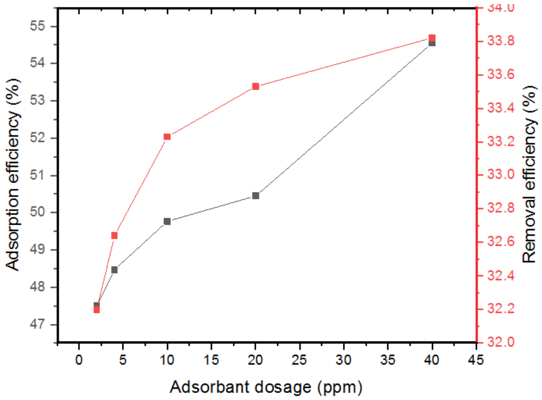

Fig. 3b. Adsorption and iron removal efficiency of flower extract incorporated Mg-MOF

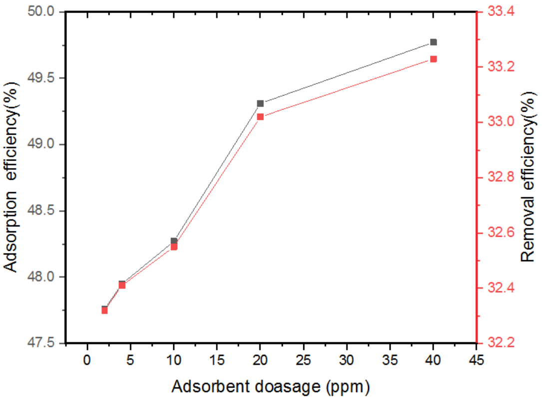

Fig. 3c. Adsorption and iron removal efficiency of leaf extract incorporated Mg-MOF

Thus, from the graphs, it is clear that on adding plant extracts, the active adsorption sites of the Mg-MOF increases. Among the prepared MOFs, flower extract added Mg-MOF was the most effective one with adsorption efficiency of 54.55% at an adsorbent dosage of 40 ppm.

Studies on mechanism of adsorption

The adsorption isotherm models explain the interaction between adsorbent and adsorbate and are important in finding the mechanisms of adsorption. The distribution of iron between water and adsorbent surface was studied using Langmuir[21] and Freundlich[22] isotherm models.

Langmuir adsorption isotherm

The Langmuir adsorption isotherm has been successfully applied to many pollutant adsorption processes from aqueous solution[23,24]. The linear form of the Langmuir model is,

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{bQ_0}$$

Where, C_e is the liquid-phase concentration of iron at equilibrium in mg/L, q_e is the amount of iron adsorbed at equilibrium in mg/L, Q_0 is the maximum monolayer adsorption capacity in mg/g, and b is Langmuir constant in L/mg or L/mol. Plots of (C_e/q_e) vs. C_e are drawn for the three prepared compounds and are shown in Figures 4(a), 4(b) and 4(c).

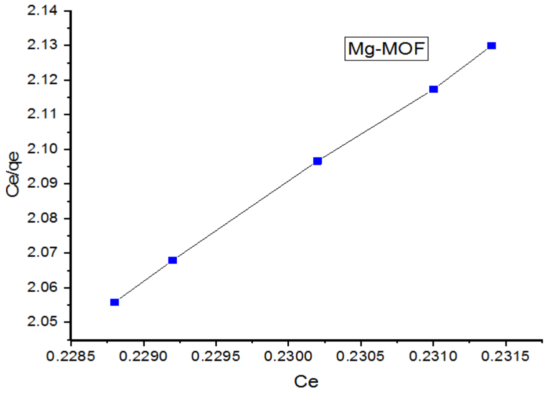

Fig. 4a. Langmuir adsorption isotherm of pure Mg-MOF

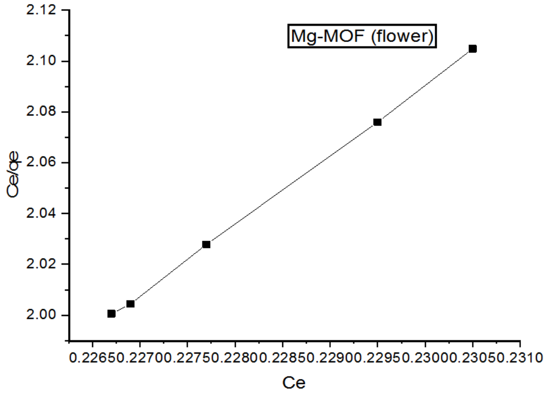

Fig. 4b. Langmuir adsorption isotherm of flower extract incorporated Mg-MOF

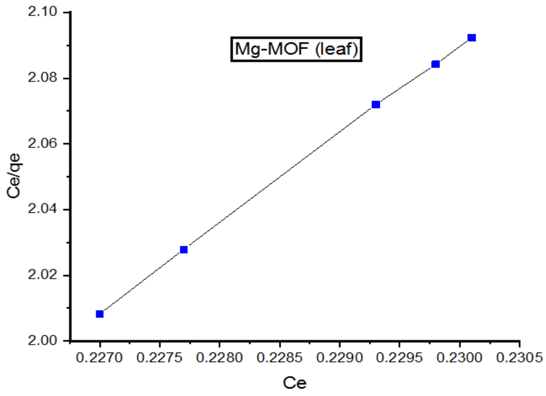

Fig. 4c. Langmuir adsorption isotherm of leaf extract incorporated Mg-MOF

The values of intercept b, slope Q_0 and the correlation coefficient R^2 were calculated. From these values the equilibrium parameter, R_L was calculated using the equation,

$$R_L = \frac{1}{1 + bC_o}$$

Where, C_0 is the initial concentration of iron[25,26]. All these values for the prepared compounds were given in Table 2.

Table 2: Langmuir adsorption parameters

Compound	Intercept b	Slope Q_0	R^2	R_L
Pure Mg-MOF	-4.39011	28.17492	0.99927	1.1
Mg-MOF with flower extract	-4.22998	27.4806	0.99958	1.05
Mg-MOF with leaf extract	-4.14828	27.12317	0.99966	1.02

All the values of R^2 were higher than 0.999 indicating that the adsorption of iron by the three prepared MOFs can be suitably explained by the Langmuir isotherm model. The values of RL indicates whether the isotherm is unfavourable, favourable or irreversible[25]. The R_L values were almost equal to one, showing a favourable, linear adsorption. These adsorption processes can be well explained by Langmuir adsorption isotherm and it happened by physisorption forming a mono layer of iron over the surface of the adsorbent.

Freundlich adsorption isotherm

Freundlich adsorption isotherm model is suitable for multi-layer adsorption. The linear form of Freundlich model is[22,27,28],

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e$$

Where q_e is the amount of iron adsorbed at equilibrium in mg/g, K_F is the adsorption capacity of the adsorbent in mg•g^{-1}, n indicates the degree to which an adsorption process is favorable and C_e is the liquid-phase concentrations of iron at equilibrium in mg/L. Both K_F and n are Freundlich constants. Plots of ln q_e vs. ln Ce for the prepared MOF samples in the adsorption study are shown in Figures 5(a), 5(b) and 5(c).

In general, as the K_F increases the adsorption capacity of the adsorbent increases. If n<1, this means poor adsorption; from one to two means moderately difficult adsorption; and from two to ten good adsorption Table 3.

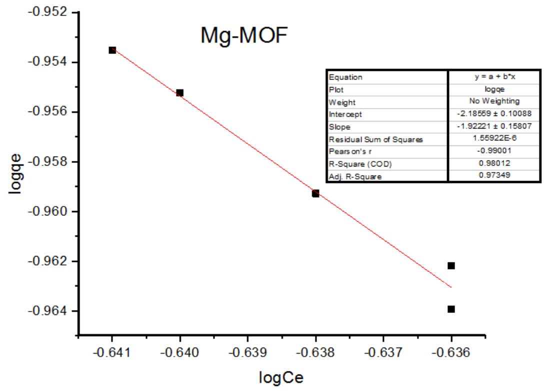

Fig. 5a. Freundlich adsorption isotherm of pure Mg-MOF

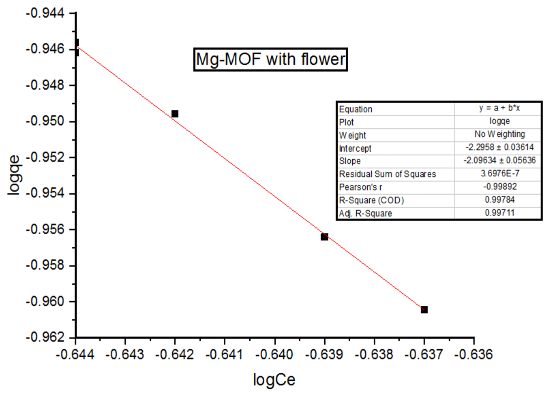

Fig. 5b. Freundlich adsorption isotherm of flower extract modified Mg-MOF

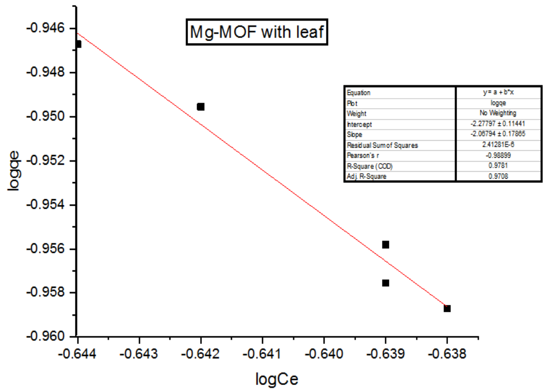

Fig. 5c. Freundlich adsorption isotherm of leaf extract modified Mg-MOF

Table 3: Freundlich adsorption parameters

Sample	Intercept	Slope	n	K_F	R^2
Mg-MOF alone	-2.18559	-1.92221	-0.5208	0.0065	0.97349
Mg-MOF (flower)	-2.2958	-2.09634	-0.4782	0.00506	0.9971
Mg-MOF (leaf)	-2.2779	-2.0679	-0.4835	0.0052	0.9708

All of the n values obtained from the Freundlich model are less than unity, indicating that poor chemisorption of iron on the MOFs. Its correlation coefficient R^2 are much lower than those for the Langmuir isotherm. It means that the Langmuir isotherm model is the best model to fit with the experimental data.

CONCLUSION

Increase in human population had increased the pollution in water bodies like rivers, lakes and even in wells. Even though majority of the population depends on municipal water supply, wells are the important source of drinking water in many rural and urban areas of Kerala, India. Metal-organic frameworks (MOFs) have the potential in water treatment sector. This is due to its eco-friendly, highly efficient and reliable water treatment nature. In this study, removal of excess iron from bore well samples was carried out using eco-friendly synthesized Mg-MOFs as adsorbent materials. Among the prepared MOFs, that modified with flower extract of Clitoria ternatea, was found to be more effective at an adsorbent dosage of 40 ppm. The adsorption process was analyzed using different isotherms and found suitable for Langmuir adsorption. Hence a mono layer of adsorption was formed on the adsorbent surface by physical adsorption. These studies pave the way for the usage of many naturally available plant materials for the drinking water treatment.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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