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Fe-MOF nanoparticles as efficient adsorbent for removal of heavy metal ions by facile hydrothermally synthesis

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Abstract:

Fe-MOFs catalyst was prepared by simple solvothermal synthesis. The Fe-MOF was characterized by XRD, TEM, SEM and FT-IR which confirmed metal organic framework nanoparticles with Nano size reached nearly 29.4 - 129.9 nm. The adsorption capacities / percentages of Fe- MOF adsorbent for heavy metals as toxic pollutants from aqueous solutions were high, which indicate that Fe-MOFs nanoparticles can be used as a good adsorbent.

Key word: Fe-MOF, Solvothermal synthesis, Adsorbent, Pollutants.

1. Introduction

Environment pollution problems have currently attracted increasing public concern with the development of industrialization and urbanization ^[1-4]. The removal of heavy metals (lead, mercury, cadmium and copper) and dyes (methylene blue) from industrial wastewaters is a major problem. Conventional methods for the adsorptive removal of inorganic and organic pollutants from wastewater include adsorption onto acidic solid catalysts ^[5-8]. Adsorption is one of the effective separation techniques to remove pollutants (heavy metal and dyes) as well as offering the potential for regeneration, recovery and recycling of the adsorbing materials ^[9-11]. During recent years, removal of heavy metal ions, both from wastewater and natural waters, has gained importance to solve and minimize the industrial and ecological waste problems. Several adsorbents such as saw dust, silica and iron oxide ^[12], sewage sludge

ash^[13], anatase - type titanium dioxide^[14], activated carbon^[15], have been used for the treatment of water from inorganic and organic pollutants .

Heterogeneous catalysts used as Nano-adsorbents for removal inorganic and organic pollutants from aqueous solution, the metal organic frameworks one of this heterogeneous nanocatalysts, Fe-MOFs having high porosity and surface area for applications for removal of organic dyes and other pollutants from aqueous solutions^[16-21]. This research aims to preparation of environmentally friendly solid acid nanocatalysts, study of structural characterization and adsorption catalytic activity of Fe-MOFs, so prepared iron-monometallic metal-organic frameworks nanocatalysts and used for adsorption of lead, mercury, cadmium and copper ions with excellent activity.

2. Preparation of Fe-MOFs nanocatalyst

The Fe-MOFs catalyst was synthesized by simple solvothermal method by mixing 1:1 molar ratio M: L: Fe (NO₃)₃.9H₂O and terephthalic acid in 40 ml DMF under vigorous stirring for 1hrs. Then addition of 2.0 ml triethylamine with stirring for 1hrs. The mixture of components was stirred for 2 hrs., after that transferred into autoclave, at 120° C for 4 hrs., MOFs precipitate was formed. The formed precipitate was filtered by centrifuge (4000 rpm), and washed, then added to chloroform (100 ml) and stood overnight. Finally, the Fe-MOFs nanoparticles were filtered and dried at 60° C in vacuum oven for 6 hrs.^[22-27].

3. Result and discussion

3.1 X-ray diffraction of Fe-MOFs nanocatalyst

All peaks of Fe-MOFs nanocatalyst were appeared at $2\theta = 5.34, 6.73, 9.63, 11.60, 12.88, 13.67, 14.80, 20.30, 23.34, 24.23, 25.25, 29.07, 34.68, 35.92, 37.49, 44.12$ and 46.25° which indicate that the Fe-MOFs nanoparticles were formed^[27-37]. The XRD shows two main peaks at 9.29 and 20.19° which are correspond to the standard pattern.^[31,32] We observed that

the peaks between 4 and 20° dominated the collected x-ray diffraction pattern. Especially, appearing of the high intensity peak below 10°, as showing in Fig. (1). the crystallite sizes of Fe-MOFs were 19.4-150.3 nm.

Fig. (1): XRD of Fe-MOFs nanocatalyst

3.2 FT-IR spectroscopy of Fe-MOFs

The broad intensity at after 3390 cm^{-1} indicates to (OH) stretching vibrations of the coordinated water-molecules^[16]. The peaks at 1580 and 1660 cm^{-1} characteristic asymmetric of COO^- group, while the peaks at 1385 and 1477 cm^{-1} characteristic symmetric of COO^- group^[17-19]. The appeared peak at $1100 - 1110\text{ cm}^{-1}$ is related to the C-O stretching vibration^[22,27]. The weak and narrow bands at $1065-1083$ and $750 - 782\text{ cm}^{-1}$ indicate to $\gamma(\text{C-H})$, $\delta(\text{C-H})$ vibration of aromatic rings which confirmed presence of BTC ligand-molecule in Fe-MOFs nanoparticles. The medium strength band of iron-oxygen (Fe-O)vibrations appeared at $538 - 557\text{ cm}^{-1}$ which proves that the iron metal organic frameworks indeed has been formed^[19, 22,23,26 ,27]. The $\Delta\nu (\nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO}))$ was 175 and 190 cm^{-1} , where it was

characteristic of the bridge coordination mode in Fe-Metal Organic Frameworks nanoparticles which proved formation of Fe-MOF, as in Fig. (2).

Fig. (2): FT-IR of Fe-MOFs nanoparticles

3.3. Transmission electron microscopy (TEM) of Fe-MOFs Nanocatalyst

TEM images results were showed irregular and similar octahedral structures, which prove that Fe-MOFs crystalline was formed with nanosize reached 30-140 nm, as showing in Fig. (3). TEM results is in accordance with XRD results. The TEM and XRD analysis confirm that Fe-MOFs nanoparticles were formed with high degree of crystallinity.

Fig. (3) : TEM images of Fe-MOFs nanoparticles

3.4 Adsorption of heavy metal ions (Pb^{2+} , Hg^{2+} , Cd^{2+} and Cu^{2+}) on Fe-MOFs nanocatalysts.

3.4.1 Effect of pollutant solutions pH on the adsorption of metal cations

pH of the pollutant (heavy metal) solutions is one of the major factors that influences on adsorption of metal ion pollutants^[37]. In general, the uptake of Pb(II), Hg(II), Cu(II), and Cd(II) pollutants on Fe-MOFs Nano-adsorbent was significantly high in basic solutions compared to acidic solutions at 100 ppm/100 ml water by 30 mg of Fe-MOFs nanocatalyst at 25° C in water bath shakers, as in Fig (4). The pH values selected in the experiments were prior to the precipitation limit of pollutants at pH=6 for cu^{2+} , at pH=5 for lead (II), at pH=7 for cadmium ions (II) and pH of mercury ions (II) was 6, but the pH at 6 for Hg(II) is not point the precipitation of Hg(II). The adsorption percentages after 6 hrs. were 86.2, 85.0, 54.2 and 64.3% for Pb (II), Hg(II), Cd(II) and Cu(II) pollutants, respectively. At acidic solutions (low pH values), low adsorption capacities were observed, due to, the hydrogen ions competing with metal ions on active sites on surface of Nanocatalyst^[38].

Fig. (4): Effect of pH of metal ions on adsorption by Fe-MOFs Nanocatalyst.

3.4.2 Effect of initial concentrations of heavy metals on the adsorption

We study effect of initial concentrations of metal pollutants on the adsorption removal rate at 25, 50, 100, 150, 200 and 300 ppm during 6 hrs. by using 30 mg of Fe-MOFs nanocatalyst at 25° C in water bath shakers. Fig. (5), shows the adsorptive removals of heavy metal pollutants. The % removal of pollutants from aqueous solutions was found to decrease with

the increase of initial concentrations of inorganic pollutants, from 25 to 300 ppm. The decreasing of adsorption capacity of heavy metals at $C_0 = 300$ ppm may be attributed to the saturation of the available active sites on surface of Fe-MOFs nanocatalyst^[40].

Fig. (5): Effect of initial heavy metals concentrations by Fe-MOFs Nanocatalysts.

3.4.3 Effect of the contact time on adsorption of heavy metals by Fe-MOFs nanocatalysts.

The adsorption efficiency as a function of contact time was monitored by varying equilibrium time between adsorbate (metal pollutants) and adsorbent (Nano-adsorbents) in the range of 0-6 hrs by Fe-MOFs^[39,.41]. The effect of contact time on adsorption of the metal pollutants from water carried out at initial concentrations of 100 ppm/10ml water at 25° C in water bath shaker by using 30 mg of Fe-MOFs as nano-adsorbent. The required equilibrium time is six hrs. The adsorption capacity of environmental metal pollutants by Fe-MOFs

observed quick increase during the first four hrs., then gradual increase till six hrs. There after no able increase in adsorption, as in Fig (6). The results indicate that the adsorption kinetics of Fe-MOF nanocatalyst was fast, due to the Fe-MOFs is microporous and so its possess high surface area^[42,43].

Fig. (6): Effect of contact time on adsorption of metal ions on Fe-MOFs nanocatalysts.

3.4.4 Effect of weight of nanocatalyst on adsorption

The adsorption of environmental metal pollutants by Fe-MOFs was studied by changing amount of the weight 10, 30, 50 and 70 mg with keeping initial concentrations 100 ppm/100ml for six hrs. at 25° C in water bath shakers on Fe-MOFS sample. The effect of weight of Fe-MOFs Nanocatalyst on the adsorption of environmental metal pollutants is

presented in Fig. (7). The results reveal that the removal percentage of the heavy metals from water increases with increase of the weight of Fe-MOF Nano-adsorbent from 10 to 70 mg. The highest adsorption removals of environmental metal pollutants were 86.20% for lead(II) 85.00% for mercury(II) 54.20% for cadmium (II) and 64.30% for copper(II), respectively. This indicate that as amount of the weight of Fe-MOFs Nano-adsorbent increases, the ability of the Fe-MOFs Nano adsorbent to adsorb of environmental metal pollutants increases, due to the Fe-MOFs nanoparticles increase with amount of nanocatalysts weight, i.e., increasing the surface area.

Fig. (7): Effect of the weight of catalysts on adsorption of heavy metals

Conflicts of interest

The authors have declared no conflicts of interest.

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Figures

Figure 1

XRD of Fe-MOFs nanocatalyst

Figure 2

FT-IR of Fe-MOFs nanoparticles

Figure 3

TEM images of Fe-MOFs nanoparticles

Figure 4

Effect of pH of metal ions on adsorption by Fe-MOFs Nanocatalyst.

Figure 5

Effect of initial heavy metals concentrations by Fe-MOFs Nanocatalysts.

Figure 6

Effect of contact time on adsorption of metal ions on Fe-MOFs nanocatalysts.

Figure 7

Effect of the weight of catalysts on adsorption of heavy metals