

Synthesis and application of Iron-Nanosilicate (Meso-Pore) for Removal of Pb(II) from Aqueous Solution

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Abstract: In this study MCM-41, Fe₂₀-MCM-41 and Fe₄₀-MCM-41 mesoporous silicates have been prepared in various conditions with cetyltrimethylammonium bromide (C16) and dodecyltrimethyl-ammonium chloride as template and various mole ratios of Si/Fe. The resulted compositions have been characterized by power X-ray diffraction, N₂ adsorption-desorption measurements and Fourier transform infrared spectroscopy (FT-IR). The Pb(II) adsorption of the MCM mesoporous type has been studied and the effect of Fe has been considered as promoter in adsorption process. Adding Fe in the MCM-41 composition has been improved some heavy metal ions adsorption considerably. Finally this adsorbents was applied to removal of Pb(II) from waste water samples.

Key words: Iron-Nanosilicate • Adsorbent • Pb(II) • MCM-41 • Isotherm

INTRODUCTION

Over recent years, there has been a noticeable increase in design, synthesis, characterization and property evaluation of zeolites and molecular sieves for catalysis, adsorption and separation, environmental pollution control [1]. IUPAC nomenclature classified these porous solids on the basis of pore size into three categories; microporous (<2nm), mesoporous (2-50nm) and macroporous (>50nm) [2].

MCM-41 (Mobile Crystalline Material) is a mesoporous silicate featuring hexagonally packed arrays of one-dimensional, cylindrical pores, with a uniform pore volume that use in the fields of adsorption, catalysis and nanotechnology due to the large specific surface area and regular porosity. The modification of the mesoporous material by various functional groups has received much attention in adsorption and separation science [3].

In this study MCM-41, Fe-MCM-41 (MCM-41 promoted by Fe) mesoporous have been prepared in various conditions with cetyltrimethylammonium bromide (C16) and dodecyltrimethyl-ammonium chloride as template [3]. For application of these compositions, heavy metals adsorption has been considered. Also, the adsorption studies of Heavy Metals on modified mesoporous iron

nanosilicate are reported. In addition, the adsorption isotherm, adsorption kinetics and the pH effect for Pb(II) have also been studied in detail. The equilibrium adsorption data are analyzed by using Freundlich and Langmuir isotherm.

Experimental

Reagents: Cetyltrimethylammonium bromide (CTAB) (C₁₆H₃₃(CH₃)₂N⁺Br), deionized water, sodium silicate, iron nitrate nonahydrate, oxalic acid and nitric acid, acetic acid, sodium acetate, sodium carbonate, and sodium bicarbonate were of analytical grade and purchased from Merck except of CTAB which was supplied by Aldrich (U.K).

Apparatus: A Philips X'pert power diffractometer system with Cu-K_α (λ=1.541 Å) radiation was used for X-ray studies. XRD analysis was performed from 1.5° (2θ) to 10.0° (2θ) at scan rate of 0.02° (2θ) sec⁻¹. Nitrogen adsorption studies were made with a Quantachrome NOVA 2200e instrument. The Nitrogen adsorption and adsorption isotherm of the adsorbent was determined at 77K and the specific surface area was determined by applying the BET equation to the isotherm [**]. The pore size distribution was calculated using the adsorption branch of the isotherm and the Barrett-Joyner-

Halenda (BJH) formula [4]. pH was measured with a Schott CG841 pH-meter (Germany). Quantitative determination of inorganic ions was made using an inductively coupled plasma-optical emission spectrometer (ICP-OES) of Varian Liberty 150- Axial. Atomic adsorption analysis was carried out by Varian AA240 and Pb (flame) method to determine Pb(II) quantity.

Preparation of Mesoporous Iron Nanosilicate: In first step, mesoporous iron nanosilicates were prepared by mixing 17.4 g CTAB (C16) with 7.2 g deionized water, this was stirred for 15 min (140 rpm), after that 3 g of sodium silicate was added to the mixture and it was further stirred for 30 min. the pH value was adjusted at 11.5 by adding nitric acid. In the second step to synthesize MCM-41, 7.6 g oxalic acid was added to the solution. It was further stirred for 15 min. the solution was kept in autoclave for 48 hr in 100 °C to prepare MCM-41. MCM-41 was calcined at 700°C for 6hr.

To prepared Fe20-MCM-41 and Fe40-MCM-41, iron nitrate (6 g and 4 g respectively) dissolved in oxalic acid (7.6 g and 3.76 respectively) and was added to MCM-41 solution. These solutions were kept in autoclave at 100 °C for 48 hr and calcined at 700 °C for 6 hr.

Procedure for Adsorption Studies: The adsorption studies of the Pb(II) ion on the Fe20-MCM-41 and Fe40-MCM-41 adsorbents were carried out using batch method. In this procedure 0.1g of adsorbent material was added to a 50 ml buffered solution of 5-20 mg L⁻¹ Pb(II) ions. The pH of the solution was adjusted with sodium acetate/acetic acid for pH 2-7 and Na₂CO₃/NaHCO₃ for pH 7-10. The suspension was stirred for a preselected period of time using a magnetic stirrer. Then it was filtered and the amount of the Pb(II) ion was determined by ICP or atomic adsorption. The percentage of Pb(II) ion that was adsorbed on the adsorbent (% uptake) was determined by comparing its concentrations before and after adsorption C_i (mg L⁻¹) and C_f (mg L⁻¹) respectively.

$$\% \text{uptake} = \frac{(C_i - C_f)}{C_i} \times 100(\%)$$

The distribution ratio (K_d) of lead and the heavy metals between the adsorbent and aqueous solution (ml g⁻¹) was also determined by following equation:

$$K_d = \frac{(C_i - C_f) \times V}{C_i \times m}$$

Where V is the volume of the initial solution and m is the mass of adsorbent material.

RESULTS AND DISCUSSION

Characterization of Adsorbent

XRD Analysis: The XRD patterns of the MCM-41, Fe20-MCM-41 and Fe40-MCM-41 (calcined) are presented in Fig.1. The XRD patterns of this materials show a strong diffraction at 2θ near 2° and 3° with the presence of small peaks that confirm the formation of mesoporous MCM-41 [5]. This result is Characteristic of hexagonal pore structure. The low-angle X-ray diffraction patterns of modified Fe20-MCM-41 and Fe40-MCM-41 indicate that the mesoporous structures of materials after modification with Fe remains intact [6].

Nitrogen Sorption Isotherm: The nitrogen adsorption isotherms and corresponding pore size distribution of the MCM-41, Fe20MCM-41 and Fe40MCM-41 are given in Figure 2 and 3. Nitrogen adsorption-desorption isotherms for MCM-41, Fe20MCM-41 and Fe40MCM-41 Showed irreversible type VI adsorption isotherms as defined by IUPAC (Figure 2). The overall shape of the adsorption-desorption isotherms remained unchanged and the pronounced steps of capillary condensation in primary mesopores were evident, indicating that the ordering of the MCM-41 support was not affected by the modification [7].

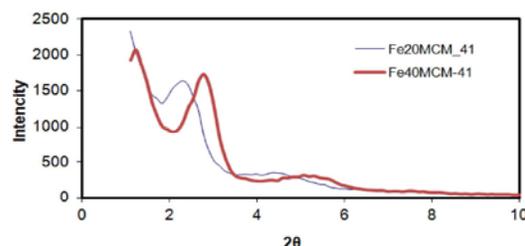


Fig. 1: XRD patterns of MCM-41, Fe20MCM-41 and Fe40MCM-41 (calcined)

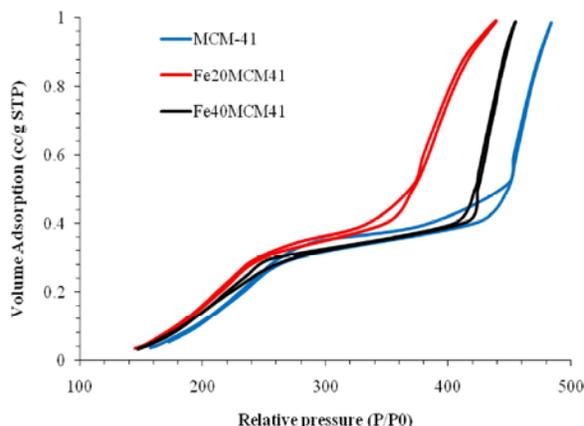


Fig. 2: BET MCM-41 components

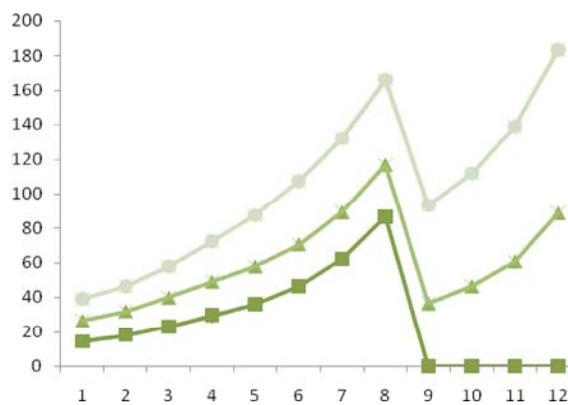


Fig. 3: Pore size distribution for MCM-41, Fe₂₀MCM-41 and Fe₄₀MCM-41

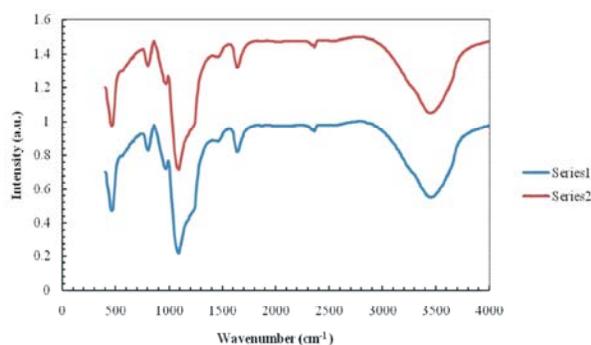


Fig. 4: FT-IR spectra of Fe₂₀MCM-41 (a) and Fe₄₀MCM-41 (b) materials

FT-IR Spectra: The FT-IR (Kbr, cm⁻¹) spectra of SBA- Fe₂₀MCM-41 and Fe₄₀MCM-41 is shown in Figure 4a and 4b, respectively. The Si-O-Si and Si-O-H stretching vibrations bands of mesoporous silica appeared at 1036, 808 and 3000-3500 cm⁻¹, respectively.

Effect of pH: pH is a vital parameter that affects adsorption process. Therefore, the pH of solution was the first optimized parameter. In several batch experiments, 0.1 g of Fe₂₀-MCM-41 or Fe₄₀-MCM-41 adsorbent was equilibrated with 50 ml of the buffer solution containing 12 mg L⁻¹ of Pb(II) ions at pH range of 2.5-8.5 for 4 h. The influence of pH variation on the retention of Pb(II) onto the modified MCM-41 is shown in Figure 5. The adsorption of Pb(II) ion varied significantly with pH of solution and the highest removal of Pb(II) was obtained in the pH of 6.5 that can be explained by the electric charges on the surface and on the Pb ion species.

Kinetic Study: Time of analysis has a profound effect on the adsorption of analytes. Therefore, the effect of shaking time of sample solution was studied. In a typical

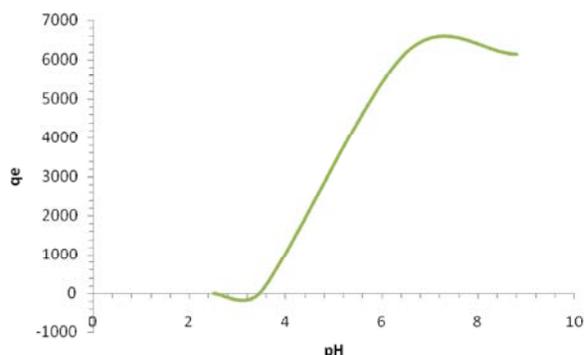


Fig. 5: Effect of pH on adsorption of Pb into the Fe₂₀MCM-41 adsorbent

kinetic test, 0.1 g of the adsorbent was added to 50 mL of 12 mg L⁻¹ of the lead solution at pH=6.5. The suspension was agitated for different periods of time (from 20 to 270 min) using magnetic mixer. The results of this study is shown in figure 5, this results showed that adsorption equilibrium is attained in the 120 min which is efficient time compared with the other adsorbent [4]. The adsorption rate suggests that the silanol groups are readily available and easily accessible probably because the uniform mesoporous channels of the Fe₂₀MCM-41 adsorbent facilitate the Pb(II) ions transportation in the process. Further investigation is still needed to understand the interaction between the adsorbate and the active site.

Adsorption Studies: The distribution coefficient of Pb(II) ion and the other heavy Metals ion on the mesoporous iron nanosilicate are increased with an increasing amount of iron in the framework of the adsorbent. It is because the incorporation of iron in the framework of MCM-41 results in an increase of the number of bronsted and the lower exentlewis acid sites [8].

Adsorption Isotherm: In the several batch experiments, 0.1 g portions of the Fe₂₀-MCM-41 adsorbent were equilibrated with varying concentrations of Pb(II) ion (initial concentrations range from 10 to 80 mg L⁻¹) at pH 6.5. The suspensions were agitated for 4h using a magnetic mixer then the supernatant solution were removed and filtered. The concentrations of Pb(II)ion in solution were determined with ICP or atomic adsorption and the amount of the adsorbed Pb(II)ion on the adsorbent were calculated from these values. The adsorption Isotherm is plotted in Figure 7. Among various binding models the Langmuir and Ferundlich

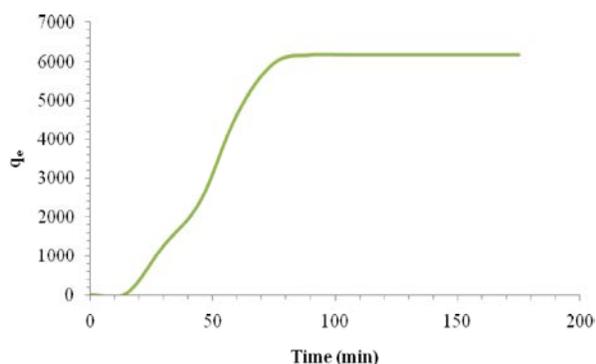


Fig. 6: Effect of contact time on adsorption of Pb(II) into the Fe20-MCM-41 adsorbent at 25°C and C_0

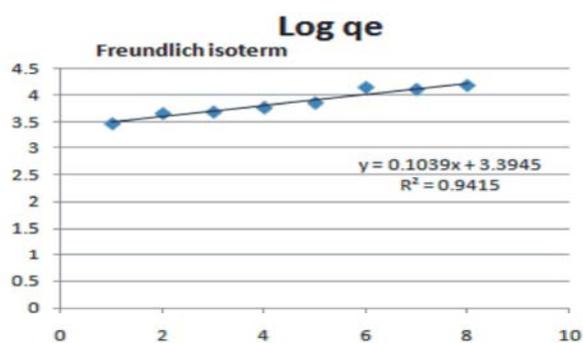


Fig. 7: Experimental adsorption data and Freundlich adsorption isotherm fit line

isotherms have been frequently employed to describe experimental data of adsorption isotherm [9-10]. From the values of R^2 the Freundlich equation provides a better fitting than the Langmuir one.

Adsorption Investigation on the Other Heavy Metals:

In this studies adsorption of the other heavy metals ions like Cu, Sm, Nd, Fe, Cd, La, Ni, Co and Cr by Fe20-MCM-41 and Fe40-MCM-41 were considered. In this consideration 0.1 g of adsorbent materials were added to a 50 ml solution that contains 5-20 mg L⁻¹ of the heavy metals ions. The pH of the solution was not changed and it was based on the material nature (without adding acid or alkali material to adjust it). Then MCM-41, Fe20-MCM-41 and Fe40-MCM-41 were separated from solution by filtration and the heavy metal ion amounts were determined by ICP or atomic adsorption. The percentage of heavy metal ions were adsorbed on the sorbents (% uptake) was determined by comparing their concentrations before and after adsorption process. The results of this study are shown in Table 1, as can be seen these materials have capability for removal of other metal ions.

Table 1: Distribution coefficients of different elements on the sorbents: [Kd value (mL g⁻¹)]

Ions	pH ^a	MCM-41	Fe ₂₀ -MCM-41	Fe ₄₀ -MCM-41
Pb	6.5	39830	39860	5430
Ni	5.43	3842.1	16000	20125
Cr	4.40	258.05	2963.23	6403.91
Co	6.75	163.05	271.27	415.74
Nd	5.65	18272.73	68333.33	14356.115
La	4.70	765.31	30500	77000
Fe	5	8638.16	16949.75	57340.9
Cd	4.37	1249.3	3871.3	10063.9
Cu	4.5	400.92	3058.7	8524.8
Sm	7.16	118346.15	52775.9	38125

^aInitial pH of each metal ion

CONCLUSION

Mesoporous iron nanosilicate (MCM-41, Fe20-MCM-41, Fe40-MCM-41) with Si/Fe mole ratio 20, 40 have been successfully synthesized by a thermal route and is a promising adsorbent for Pb(II) ion and heavy metal removal from aqueous solution. The modification of MCM-41 by iron ion is rapid, simple and inexpensive method compared with the modification by organic modifiers. The high content of silanol groups and the excellent properties of Mesoporous iron nanosilicate endow the adsorbent with an improved adsorption ability 39860 mg L⁻¹ and fast kinetics for less than 120 min for Pb(II) [11-12].

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