Enhancement of adsorption capacity of low cost mesoporous MCM-41 and their antibacterial and antifungal activities

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Abstract
This work aims to the enhancement of low cost MCM-41 adsorption capacity of copper and iron ions separately and as a mixture from solution and subsequently their use in antibacterial and antifungal activities. MCM-41 mesoporous were synthesized from used spent glass as source of silicon and aluminum. The hybrid MCM-41 mesoporous were obtained by impregnation of 5-sulfonic acid on the MCM-41 pores under different mass ratios (5, 10, 15, 20 and 25%). The hybrid solids were characterized by x-ray diffraction (XRD), and the presence of 5-sulfonic acid in hybrid MCM-41 is verified by thermogravimetric analysis and infrared spectroscopy. The effect of contact time, initial pH of a solution, heavy metal concentrations and 8-hydroxyquinoline 5-sulfonic acid content on the adsorption efficiency were investigated. Pseudo-first/second order isotherms are applied to determine the efficiency of hybrid solid. The experimental data fitted well with the pseudo-second order model for Cu$^{2+}$ and Fe$^{3+}$ adsorption. Maximum yields for Cu$^{2+}$ and Fe$^{3+}$ were 94% and 95% respectively. However, the extraction yield for both ion metals seems to be increase to reach 98.24% and 95.10% for iron and copper respectively when both solutions are mixed together. The hybrid MCM-41 with higher extraction yield for both metal ions and for mixture are applied as antibacterial inhibitors against Gram-negative (E. coli ATCC 25922, P. aeruginosa ATCC 27853), Gram-positive (S. aureus1 ATCC 25923, S.aureus2 ATCC 43300) bacteria and also as antifungal against Candida albicans ATCC 10231. The obtained results of the application of hybrid MCM-sox Cu, Fe and Cu/Fe as antibacterial and antifungal inhibitors seem to be very promising material in the adsorption and antimicrobial fields.

1. Introduction

The main causes of environmental pollution are linked to heavy metals and pathogenic microorganisms. Heavy metals are a serious hazard to the environment, such as the aquatic ecosystem, due to their accumulated in an ecological system to induce irreversible pollution or in the human body. In addition, microbial contamination has always been a challenge that threatens the health of humans. Many types of bacteria can cause serious life-threatening infections in humans. Therefore, it is important and necessary to develop an efficient, inexpensive and environmentally friendly material capable of either adsorbing or trapping these metals and has both an antibacterial and an antifungal effect. From a health, environmental and economic point of view the elimination of these toxic metals is very important and has a crucial issue. Diverse processes were improved to minimize this environmental problem, such as chemical precipitation [1], heavy metal chelating precipitation [2, 3], membrane filtration [4], activated carbon [5], reverse osmosis [6], and ion exchange treatment[7, 8], all of which...
can be effective in removing copper and iron from aqueous system. Unfortunately, the high cost and complexity of procedures is diverting researchers to other procedures to separate these metals from the environment and to make them useful for potential antibacterial activities [9, 10]. Many studies used phyllosilicates [11, 12] and microporous materials in the adsorption of different metals ions [13, 14] due to their higher cationic exchange capacity instead of mesoporous materials which have drawbacks in terms of cation exchange capacity (CEC) and exorbitant costs. In spite of all these troublesome characteristics, the mesoporous materials have other advantages, such as identical mesoporous sieves ranging from 2 to 10 nm, and higher surface areas up to 1000 m$^2$ g$^{-1}$ [15–17]. This paper will describe the procedure for low-cost synthesis of MCM-41 mesoporous materials from spent waste and how they will be used as adsorbed and antimicrobial metal promoters. On the basis of a literature review, there is only a few documents [18] on the use of 8-hydroxyquinoline for the elaboration of fluorescent materials. This study treats the use of 8-hydroxyquinoline mesoporous MCM-41 hybrid (MCM-sox) for simultaneous investigation of the removal of copper and iron metals ions and their applications in antimicrobial activities. The mesoporous MCM-41 were prepared from waste spent glass as silicon and aluminium sources instead of lab reagents such as Ludox and sodium aluminates respectively to reduce significantly the synthesis cost of MCM-41 to be used as trap of ion metals for an antibacterial and antifungal possible activities.

## 2. Experimental

### 2.1. Reagents and solutions

#### 2.1.1. Mesoporous reagents

The spent glass used in this is recovered from municipal waste their chemical compositions are listed in Table 1. The other reactants applied in this work were cetyltrimethylammonium bromide (C$_{16}$H$_{33}$NBr, CTAB, Aldrich; 99%) as surfactant, and Ammonium hydroxide, 25% (NH$_3$, 99.99%, Aldrich) and acetic acid (HNO$_4$, 99.8% Aldrich) and 8-hydroxyquinoline 5-sulfonic acid (sox, Aldrich).

#### 2.1.2. Adsorption reagents

The Cu$^{2+}$ and Fe$^{3+}$ (0.1 g L$^{-1}$) solutions were prepared from their corresponding salt (CuCl$_2$.2H$_2$O, FeCl$_3$.4H$_2$O) in deionised water. NaCl and HCl were also used. Spent glass was used as silicon and aluminium sources for the synthesis of MCM-41 according to the process given by Adjdir et al [19]. To extract the Si and Al needed to synthesis MCM-41 from waste spent glass, a fusion process at 550°C was adopted which consisted of a treatment of sodium hydroxide with waste spent glass under a mass ratio of 1:1.2, waste spent glass: NaOH to obtain a fused mass which was cooled at room temperature overnight then mixed with water at mass ratio fused mass: H$_2$O (1:6) and stirred overnight at room temperature. After centrifugation of the mixture, liquid solution obtained is called supernatant its elemental compositions are given in Table 2. The synthesis procedure of Al-MCM-41 from the supernatant was given as follows [19]. 0.867g of hexadecyltrimethylammonium bromide (C$_{16}$TMABr), different mass ratios 5, 10, 15, 20 and 25% of 8-hydroxyquinoline 5-sulfonic acid (sox), 15 ml water and 0.75 g NH$_4$OH were combined with 40 ml of supernatant separately and stirred at room temperature for 12 hours.

### Table 1. Elemental compositions of Bentonite and waste spent glass in weight %.

| Composition     | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | K$_2$O | MgO | Na$_2$O | SO$_3$ | L.O.I |
|-----------------|---------|-------------|-------------|-----|--------|-----|---------|--------|------|
| Waste spent glass | 71.92   | 0.972       | 0.085       | 8.93| 0.55   | 4.45| 13.2    | 0.21   | 0.07 |
| Bentonite [19]  | 65.20   | 14.10       | 2.30        | 1.35| 0.8    | 2.20| 1.15    | 0.21   | 12.69|

### Table 2. Elemental compositions of supernatant of Bentonite and waste glass by ICP-OES.

| Element | Supernatant (mg L$^{-1}$) |
|---------|--------------------------|
| Na      | 56 400                   |
| Si      | 10 600                   |
| Al      | 645                      |

| Element | Supernatant (mg L$^{-1}$) |
|---------|--------------------------|
| Na      | 54 400                   |
| Si      | 26 450                   |
| Al      | 145                      |

Table 1. Elemental compositions of Bentonite and waste spent glass in weight %.

Table 2. Elemental compositions of supernatant of Bentonite and waste glass by ICP-OES.

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then an appropriate amount of acid acetic was added. The obtained hydrogels were treated at 100 °C in glass tube instead of autoclave for 48 h. The solids obtained were called WSG-MCM-41-sox (scheme 1).

2.2. Characterization methods
Inductively Coupled Plasma Optical Emission spectrometer (ICP-OES) was used to determine elemental composition of supernatant solutions. Formation and structure of Al-MCM-41 was checked by XRD. Diffraction patterns were recorded in the 2θ range of 1–70° with a step of 0.02° 2θ and a step time of 5 s on a Bruker D5000 diffractometer with CuKα (λ = 1.5406 Å) radiation (40 kV, 40 mA). The copper and iron ions concentrations were determined by Perkin–Elmer flame atomic absorption spectrometer, Model 2380.

2.3. Metal extraction procedure
In batch experiments at 25 °C, the adsorption of Cu (II) and Fe (II) (0.1 g l⁻¹) was performed. 0.1 g of MCM-41-sox samples was mixed mechanically in polypropylene tubes with 10 ml of aqueous metal solution during 180 min separately. The equilibrium pH was determined after phase separation. The concentrations of metal ions were calculated by atomic absorption spectroscopy on a Perkin–Elmer 2380 spectrophotometer.

2.4. Kinetics adsorption procedure
The kinetic study was carried out under the following experimental conditions: 0.1 g of MCM-41-sox mesoporous material is suspended in 10 ml of Cu (II) and Fe (II) solutions at 25 °C for contact times ranging from 0 to 360 min separately. Two kinetic models pseudo-first and pseudo-second order have been applied to understand the adsorption behaviour.

2.5. Cu/Fe selectivity separation
To study the adsorption selectivity between iron and copper ions, an appropriate amount of MCM-41-sox solid was mixed with 100 mg l⁻¹ of a solution containing Cu (II) and Fe (II) at pH 4 corresponding to Cu (II) and Fe (II) solutions respectively.

2.5.1. Preparation of bacterial cultures
The same method as presented in previous work [10] was used to prepare the bacterial medium. The adsorbents materials MCM-sox, MCM-sox-Cu15%, MCM-Sox-Fe15% and MCM-sox-Fe/Cu15% were tested on the inhibition of bacteria. A same amount of these materials are deposited on the surface of solid mass medium seeded with pure bacterial culture. The studied pathogenic bacteria are Staphylococcus aureus ATCC 25923, Escherichia coli ATCC 25922, Staphylococcus aureus ATCC 43300, Pseudomonas aeruginosa ATCC 27853 and for antifungal activity against Candida albicans ATCC 10231 was used. 0.5 ml culture (10⁶ cell ml⁻¹) acquired after incubation at 37 °C for 24 h was mixed with 10 ml of medium (PDA) liquid at 40 °C. This last is melted by heating and then cooled before placing in contact with the microbial suspension. The mixture was deposed in Petri dishes of 90 mm. Discs materials exchanged by copper, iron and both copper and iron previously sterilized at 180 °C for 30 min, and are then putted in the medium containing the bacteria. The antimicrobial activity is determined after incubation of the dishes in an oven at 37 °C for 24 h for bacteria and 48 h at 30 °C for Candida albicans. The inhibition zone for bacterial growth was detected visually and photographed.
3. Results and discussion

3.1. Solid characterizations

3.1.1. Inductively coupled plasma optical emission spectrometer (ICP-OES)

The ICP-OES analysis (table 2) reveals differences between supernatant resulting from waste spent glass and Bentonite \[20, 21\]. The amount of silicon drawn by the alkaline fusion method of waste spent glass is about 26 450 mg l\(^{-1}\) which seems much higher than that extracted from Bentonite 10 600 mg l\(^{-1}\), and the difference is around 46%. By contrast, the amount of aluminum drawn from Bentonite \[20\] is ca 645 mg l\(^{-1}\), higher to that found from waste spent glass is 145 mg l\(^{-1}\). The huge amount of silicon extracted from the waste spent glass can be explained either by the element composition of glass, where the main element that constitutes the waste spent glass is silica.

3.1.2. X-rays diffraction

The powder XRD patterns of the Al-MCM-41 synthesized from waste spent glass are depicted in scheme 2 and figure 1(a). The XRD pattern of all samples display a higher crystalline order and present the same reflections which consist of one very strong peak (100) and two weak reflections corresponding to (110), and (200) at 2\(\theta\).
ranging from 2° to 6°. The (100) reflection which characterized a hexagonal pore structure of Al-MCM-41 was observed in the low-angle x-ray patterns [19, 22, 23]. 

Based on the XRD of both samples in figure 2(b), it can be noted that the sample synthesized from waste spent glass has a better crystallinity in comparison to that one synthesized from Bentonite [24]. This is related to the aluminum content in Bent-MCM framework Si/Al ca. 16 and in WSG-MCM framework Si/Al ca. 182 (table 2) [20]. According to the XRD of the samples, it is concluded that the samples synthesized from waste spent glass present an additional distinct peaks in the region of 2θ ranging from 20° to 25°, these peaks are attributed to the crystalline NaNO3. The existence of this new phase, that do not belong to MCM-41 phase, is due to the interaction of HNO3 acid added in the synthesis step to decrease the pH of the supernatant with the excess of Na⁺ from the alkaline fusion step. In this work the excess of Na ions are generated into the new crystalline NaNO3 phase. However, the Gaussian conforms the existence of an amorphous silica phase. This indicates that the amount of silica used in the synthesis could be greater than the necessary amount.

3.1.3. Infrared spectroscopy analysis
The FTIR spectrum of MCM-41-sox shows a broad band in the region 3438–3414 cm⁻¹ attributed to the surface elongation vibrations of the silanol groups (Si-OH) [25]. The peaks at 2925 and 2854 cm⁻¹ are attributed to C–H stretching vibration of cetyltrimethylammonium and 8-hydroxyquinolene5-sulfonic acid (sox). A strong peak in the region 1245–1020 cm⁻¹ denotes C–O stretching vibrations. The MCM-41-sox shows the asymmetric and symmetric S=O stretching vibration in the region 1390–1368 cm⁻¹ and 1168–1150 cm⁻¹. the peak at 1620 cm⁻¹ is attributed to C=C stretching in aromatic nuclei of 8-hydroxyquinoline 5-sulfonic acid (sox) [18]. The deformation vibrations mode of adsorbed water molecules causes the appearance of an average band around 1633 cm⁻¹. The bands observed at 1006–1280 cm⁻¹ correspond to the asymmetric elongation vibration of the Si-O-Si and Si-O-Al bonds, the absorption band in the region 430 and 517 cm⁻¹ corresponds to the vibration of deformation of the Si–O⁻ and Al–O⁻ bonds [26, 27] figure 2.

3.1.4. Scanning electron microscopy
The SEM images of the particle morphology and size of the WSG-MCM-41 sample was presented in (figure 3). The WSG-MCM-41 sample exhibits a silica fibers or nanotubes. This evidently, the detailed experimental conditions such as the amounts of silicon and aluminum and the acid concentration in the self-assembly reaction play an important role in the determination the particle shape and the particle size. The obtained morphology is similar to that found by Adjdir and coworker [19] where they stated that when the content of aluminum into MCM-framework decrease, the obtained morphology tends to a nanotube shape. In the Bent-MCM-41 sample, the morphology is more spherical than nanotube, This is due to aluminum, which seems to block the Si polymerization sites, thus leading to a reduced growth in all dimensions. This nanotube morphology is also observed when the Si-MCM-41 is synthesized from laboratory reagents in absence of aluminum. This phenomenon can be explained by the process of polymerization between different silica species which leads to
the strengthening of the silica walls and to the improvement in the long-range ordering. This result is confirmed by XRD.

### 3.2. Metal extraction

The reaction of divalent metals adsorption by MCM-sox-15% is given below [11]

\[
M^{2+} + 2HL \rightleftharpoons ML_2 + 2H^+ \quad \text{(Reaction 1)}
\]

Where \( M \) represents the metal species and \( HL \) represents the sox ligand.

The Cu(II) or Fe(II) adsorption from aqueous solution by MCM-sox was studied under different extraction parameters.

The metal extraction percentage \( E\% \), can be given by equation (1):

\[
E\% = \left( \frac{n_{M_{eq}}}{n_{M_{aq,i}}} \right) \times 100
\]

Where \( n_{M_{eq}} \) is the total number of metal moles in the solid phase at equilibrium and \( n_{M_{aq,i}} \) is the initial total number of metal moles in the aqueous phase respectively. It is found from the analytical concentrations of the metal ion in the aqueous phase before and after adsorption ([M\(_{aq,i}\)]) and ([M\(_{aq,e}\)]) respectively:

\[
E\% = \left( \frac{[M_{aq,i}] - [M_{aq,e}]}{[M_{aq,i}]} \right) \times 100
\]

#### 3.2.1. Effect of stirring time and kinetic of adsorption

The determination of the effect of stirring time on the extraction yields at pH 4 was studied and given in figure 4. It can be noticed from this plot that the maximum of extraction yield are around 93.87% for Fe(II) and 81.41% for Cu(II) and it is reached after 60 min. Therefore, the contact time of 60 min was adopted for subsequent studies of both ion metals. For the kinetic adsorption, two models are chosen the pseudo-first order expressed in equations (3), (4) and the pseudo-second order given in equations (5), (6) to investigate the kinetic order of the extraction process [28].

For a pseudo-first order reaction (figure 5), the rate law is expressed by equation (3):

\[
\frac{dq_t}{dt} = k_1 (q_e - q_t)
\]

Where:
- \( k_1 \): the rate constant expressed in (min\(^{-1}\)),
- \( q_e \): quantity of the metal ion extracted at equilibrium (mmol g\(^{-1}\)),
- \( q_t \): quantity of the metal ion extracted at time \( t \).

After integration equation (4) is obtained

\[
\ln (q_e - q_t) = \ln q_e - k_1 t
\]
The rate law for pseudo-second order reaction (figure 6) is expressed by equation (5)

\[
d\hat{q} / dt = k_2(q_e - \hat{q})^2
\]

(5)

Where \(k_2\) is the rate constant (g/mmol.min)
The obtained results clearly shown that, in general, the retention of Cu(II) increases as the mass ration of the sox increases. These results are in agreement with those find by many researchers and can be related to the nature of the sox. Moeller et al. [36] stated that the pore structure of granular activated carbon and chemistry of the ligand molecule (as chelating agents) probably contribute significantly towards uptake of copper ions and concluded that sox ligand behaves as a bidentate (N, O) ligand and thus could chelate effectively with metal ions like copper and iron. However, the best results are attributed to Fe(II), where de retention yields are higher in all mass ratios.

3.2.4. Adsorption selectivity effect of Cu(II) and Fe(II) by MCM-41-sox 15%

Two solutions containing copper and iron were prepared at 100 mg L\(^{-1}\) separately then mixed together for a while. An amount of MCM-41-sox was added to the mixture under stirring for 60 min at 25 °C for pH4. From the results given in table 6 both ions are practically extracted at pH4. MCM-41-sox seems to have an affinity
towards iron and copper. The extraction yield of iron is very close to copper around 98.24% and 95.10% respectively.

4. Antimicrobial and antifungal tests

The antibacterial activity against Gram-negative (E. coli ATCC 25922, P. aeruginosa ATCC 27853, ), Gram-positive (S. aureus1 ATCC 25923, S.aureus2 ACC 43300) bacteria and also as antifungal against Candida albicansATCC 10231 for the adsorbents was evaluated as showed in the figure 7. The diameters of inhibition zones were recorded in table 7. MCM-sox presents no antibacterial activity versus the microorganisms. The same result was also observed in the case of zeolites and clay mineral used alone [37–39]. The adsorbents samples MCM-sox-Cu15% and MCM-sox-Fe15% presented the excellent antibacterial activity against gram-positive bacteria. However, in the case of Gram-negative bacteria only the antibacterial activity of MCM-sox-Fe15% adsorbent was observed. In the case of MCM-sox-CuFe15%, the antibacterial activity has been greatly improved and has shown an obvious synergistic antibacterial effect, this is probably due to both copper and iron ions which show some antibacterial activity [39, 40], but also to attack targets against microorganisms may be
different from each other. A weak antibacterial activity was observed for the adsorbents studied against *Escherichia coli* ATCC 25922. This shows a very great resistance of this bacteria. However, MCM-sox-Cu15% presents no activity antifungal against *Candida albicans* ATCC 10231. Unlike the result found by MCM-sox-Cu15%, MCM-sox-Fe15% presents an activity antifungal. This activity seems to be increased when MCM sox contained both metal ions (MCM-sox-CuFe15%).

### 5. Conclusion

The summary of this work was the removal of divalent metals using hybrid MCM-41-sox mesoporous materials and their uses against antibacterial and antifungal. In this study, the removal of Cu$^{2+}$ and Fe$^{2+}$ using hybrid MCM-41-sox mesoporous materials type synthesized from used spent glass is successfully undertaken. Hybrid MCM-41 with different mass rations of sox were synthesized, the intercalation of the sox molecules in the pores of the mesoporous during the synthesis did not affect the structure of the MCM-41. The adsorption of Cu$^{2+}$ and Fe$^{2+}$ from aqueous solutions on MCM-41-sox 15% is well described and fit with the pseudo-second order kinetic model. The remediation yield of bivalent metals copper and iron is up to 90% for both ions. The hybrid MCM-sox-Cu15% and MCM-sox-Fe15% presented an excellent antibacterial activity. In the case of MCM-sox-CuFe15%, the antibacterial activity has been greatly improved and has shown an obvious synergistic antibacterial effect. However, MCM-sox-Cu15% presents no activity antifungal against *Candida albicans* ATCC 10231. Unlike the result found by MCM-sox-Cu15%, MCM-sox-Fe15% presents an activity antifungal very promising. This activity seems to be increased when MCM sox contained both metal ions (MCM-sox-CuFe15%).
References

[1] Ku Y and Jung I-L 2001 Photocatalytic reduction of Cr (VI) in aqueous solutions by UV irradiation with the presence of titanium dioxide Water Res. 35 135–42
[2] Matlock M M, Henke K R and Atwood D A 2002 Effectiveness of commercial reagents for heavy metal removal from water with new insights for future chelate designs J. Hazard. Mater. 92 129–42
[3] Ying X and Fang Z 2006 Experimental research on heavy metal wastewater treatment with dipropyl dithiophosphate J. Hazard. Mater. 137 1636–42
[4] Landaburu-Aguirre J, García V, Pongrácz E and Keiski R L 2009 The removal of zinc from synthetic wastewaters by micellar-enhanced ultrafiltration: statistical design of experiments Desalination 240 262–9
[5] Yanagisawa H, Matsumoto Y and Machida M 2010 Adsorption of Zn (II) and Cd (II) ions onto magnesium and activated carbon composite in aqueous solution Appl. Surf. Sci. 256 1619–23
[6] Zhang L, Yanjun W, Xiaoyan Q, Zhenhuan L and Jinren N 2009 Mechanism of combination membrane and electro-winning process on treatment and remediation of Cu^{2+} polluted water body J. Environ. Sci. 21 764–9
[7] Abo-Farha S, Abdel-Aal A, Ashour I and Garamon S 2009 Removal of some heavy metal cations by synthetic resin purulite C100 J. Hazard. Mater. 169 190–8
[8] Motsi T, Rowsom N and Simmons M 2009 Adsorption of heavy metals from acid mine drainage by natural zeolite Int. J. Miner. Process. 92 42–8
[9] Kebir Z A M, Mokhtar A, Adjdir M, Benguedda A and Sassi M 2018 Preparation and antibacterial activity of silver nanoparticles intercalated kenyaite materials Mater. Res. Express 5 058021
[10] Zahraroua M, Mokhtar A, Adjdir M, Bennabi F, Khaled R, Djelad A, Benguedda A and Sassi M 2018 Preparation of Al-magadite material, copper ions exchange and effect of counter-ions: antibacterial and antifungal applications Res. Chem. Intermed. 45 653–44
[11] Bouzza D, Miloudi H, Adjdir M, Tayeb A and Boos A Competitive adsorption of Cu (II) and Zn (II) on impregate raw Algerian bentonite and efficiency of extraction Appl. Clay Sci. 151 2018 118–23
[12] Boudahri M, Bouzza D, Adjdir M, Miloudi H, Abdelkader N and Tayeb A 2018 Remediation of copper ions from aqueous solution using hybrid magadite: kinetics, isotherm and mechanism of removal Res. Chem. Intermed. 44 6103–17
[13] Erdem E, Karapinar N and Donat R 2004 The removal of heavy metal cations by natural zeolites J. Colloid Interface Sci. 280 309–14
[14] Hui K, Chao C Y H and Kot S 2005 Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled fly ash J. Hazard. Mater. 127 69–101
[15] Adjdir M, Ali-Dahmane T and Weidler P 2009 The structural comparison between Al-MCM-41 and B-MCM-41 C.R. Chim. 12 793–400
[16] Chen C-Y, Li H-X and Davis M E 1993 Studies on mesoporous materials: I. Synthesis and characterization of MCM-41 Microporous Mater. 2 17–26
[17] Inagaki S, Fukushima Y and Kuroda K 1993 Synthesis of highly ordered mesoporous materials from a layered polysilicate J. Chem. Soc., Chem. Commun. 8 680–2
[18] Fazaéli Y, Amini M M, Mohajerani E, Sharbatdaran M and Torabi N 2010 Grafting aluminum (III) 8-hydroxyquinoline derivatives on MCM-41 mesoporous silica for tuning of the light emitting color J. Colloid Interface Sci. 346 384–90
[19] Adjdir M, Ali-Dahmane T, Friedrich S, Scherer T and Weidler P 2009 The synthesis of Al-MCM-41 from volclay—A low-cost Al and Si source Appl. Clay Sci. 46 185–9
[20] Adjdir M, Bennadouch C K, Benahoua H, Kaid M, Karmouzi M, Boudina M and Weidler P 2015 Increasing the efficiency of silicon and aluminum extraction from Volclay by a water iteration treatment for the synthesis of MCM-41 nanomaterials C.R. Chim. 18 385–90
[21] Berk Z 2008 Food Science and Technology: International Series ed Z Berk (Academic Press, City) 624 9780080920238
[22] Luan Z, Cheng C-F, Zhou W and Klinowski J 1995 Mesopore molecular sieve MCM-41 containing framework alumnum J. Phys. Chem. 99 1018–24
[23] Beck J S, Vartull J, Roth W J, Leonowicz M, Kresse C, Schmitt K, Chu C, Olson D H, Sheppard E and McCullen S 1992 A new family of mesoporous molecular sieves prepared with liquid crystal templates JACS 114 10834–43
[24] Ali-Dahmane T, Adjdir M, Hamacha R, Villieres F, Benguedda A and Weidler P 2014 The synthesis of MCM-41 nanomaterial from Algerian Bentonite: the effect of the mineral phase contents of clay on the structure properties of MCM-41 C.R. Chim. 17 1–6
[25] Villegas M F, Garcia-Urioestegui L, Rodriguez O, Izquierdo-Barba I, Salinas A J, Toriz G, Valtier-Regi M and Delgado E 2017 Lysine-Grafted MCM-41 silica as an antibacterial biomaterial Bioengineering 4 80
[26] Sirotin S V, Moskovskaya I F and Romanovsky B V 2011 Synthetic strategy for Fe-MCM-41 catalyst: a key factor for homogeneous or heterogeneous photon oxidation Catalysis Sci. & Technology 1 971–80
[27] Sirotin S, Moskovskaya I, Kolyagin Y G, Yatsenko A and Romanovsky B 2011 Iron (III) chloride supported on MCM-41 molecular sieve as a catalyst for the liquid-phase oxidation of phenol Russ. J. Phys. Chem. A 85 390–6
[28] Gupta B S, Curran M, Hasan S and Ghosh T 2009 Adsorption characteristics of Cu and Ni on Irish peat moss J. Environ. Manage. 90 954–60
[29] Azizian S 2004 Kinetic models of sorption: a theoretical analysis J. Colloid Interface Sci. 276 47–52
[30] Azizian S 2006 A novel and simple method for finding the heterogeneity of adsorbents on the basis of adsorption kinetic data J. Colloid Interface Sci. 302 76–81
[31] Karabulut S, Karabakan A, Denizli A and Yürüm Y 2000 Batch removal of copper (II) and zinc (II) from aqueous solutions with low-rank Turkish coals Sep. Porif. Technol. 18 177–84
[32] Abollimo O, Aceto M, Malandrino M, Sarzanini C and Mentasti E 2003 Adsorption of heavy metals on Na-montmorillonite. Effect of pH and organic substances Water Res. 37 1619–27
[33] Chaiyasith S, Chaiyasith P and Septhum C 2006 Removal of cadmium and nickel from aqueous solution by adsorption onto treated fly ash from Thailand J. Sci. Technol. 11 2
[34] Malandrino M, Abollino O, Giacomino A, Aceto M and Mentasti E 2006 Adsorption of heavy metals on vermiculite: influence of pH and organic ligands J. Colloid Interface Sci. 299 537–46
[35] Chen C-Y, Chiang C-L and Chen C-R 2007 Removal of heavy metal ions by a chelating resin containing glycine as chelating groups Sep. Purif. Technol. 54 396–403
[36] Moeller T and Ramaniah M V 1954 The chemistry of thorium. VI. 1 Some observations on the 5, 7-Dihalo-8-quinolinol chelates of thorium JACS 76 2022–4
[37] Rivera-Garza M, Olguin M, Garcia-Sosa I, Alcántara D and Rodríguez-Fuentes G 2000 Silver supported on natural Mexican zeolite as an antibacterial material Microporous Mesoporous Mater. 39 431–44
[38] Top A and Ulkül S 2004 Silver, zinc, and copper exchange in a Na-clinoptilolite and resulting effect on antibacterial activity Appl. Clay Sci. 27 13–9
[39] Tan S Z, Zhang K H, Zhang I L, Xie Y S and Liu Y L 2008 Preparation and characterization of the antibacterial Zn$^{2+}$ or/and Ce$^{3+}$ loaded montmorillonites Chin. J. Chem. 26 865–9
[40] Yunhua Y, Guangjian D, Shaozao T, Yingliang L, Qingshan S and Ouyang Y 2011 Structure and synergetic antibacterial effect of zinc and cerium carried sodium zirconium phosphates J. Rare Earths 29 308–12