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## **Novel insights in Al-MCM-41 precursor as adsorbent for regulated haloacetic acids and nitrate from waters**

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## **Abstract**

High concentration of  $\text{NO}_3^-$  in groundwater has raised concern over possible contamination of drinking water supplies. In addition, the formation of haloacetic acids (HAAs) as by-products during disinfection with chlorine based agents is still a relevant issue, since HAAs pose serious health hazard. In this work, we investigated the affinity of a precursor of Al-MCM-41 (a mesostructured hexagonal alumino-silicate containing the template surfactant) towards nitrate and HAAs, for its possible application in the removal of these pollutants from natural and drinking waters. Additionally, adsorption kinetics and isotherms were studied.

The adsorbent was synthesized using cetyltrimethylammonium bromide as surfactant and characterized by physical-chemical techniques. Simulated drinking water was spiked with the EPA regulated HAAs (monochloroacetic MCAA, monobromoacetic MBAA, dichloroacetic DCAA, dibromoacetic DBAA, trichloroacetic TCAA acids) and placed in contact with the adsorbent. The effect of matrix composition was studied. Adsorption kinetic studies were performed testing three kinetics models. For the adsorption studies, three adsorption isotherm approaches have been tested to experimental data. The pollutant recoveries were evaluated by suppressed ion chromatography (IC).

The affinity of the adsorbent was  $\text{TCAA}=\text{DBAA}=\text{DCAA}>\text{MBAA}>\text{MCAA}$  with DCAA, DBAA and TCAA completely removed. A removal as high as 77% was achieved for 13 mg/L nitrate. The adsorption isotherms of  $\text{NO}_3^-$  and monochloroacetic acid can be modeled by the Freundlich equation, while their adsorption kinetics follow a pseudo-second order rate mechanism.

The adsorbent exhibited high affinity towards HAAs in simulated drinking water even at relevant matrix concentrations, suggesting its potential application for water remediation technologies.

**Keywords:** haloacetic acids, nitrate, removal, Al-MCM-41, natural and drinking waters, adsorption kinetics, adsorption isotherm

## 1. Introduction

The quality of waters intended for human consumption as well as of natural waters is still a current environmental and human health concern.

Water disinfection, although ensuring sanitation and safe bacteriological quality of drinking water, leads to the formation of the so called disinfection by-products (DBPs).

Under the term DBPs are included groups of organic and inorganic compounds formed during water disinfection by reactions of disinfectants with natural organic matter (humic, fulvic acid) and bromide or iodide, if present, in water source. Among DBPs, haloacetic acids (HAAs) are halogenated derivatives of acetic acid and they are formed, during potabilization, by reaction of organic material with the chlorine-based disinfection agents. HAAs represent the second largest group of DBPs (after trihalomethanes) generated by water disinfection and their presence has been linked to possible health threats by numerous toxicological studies (Pals et al. 2011).

At present, five HAAs (monochloroacetic MCAA, monobromoacetic MBAA, dichloroacetic DCAA, dibromoacetic DBAA, trichloroacetic TCAA acids) are regulated under the Stage 2 Disinfectant (D)/DBP Rule released by U.S. EPA (January 2006). The regulated HAAs are usually referred to as HAA5. The limits imposed for the sum of HAA5 is 60 µg/L. European Commission is currently working on a drinking water safety plan, with a proposed parametric value of 80 µg/L for the total nine HAAs (Harman et al. 2011).

Many monitoring programmes prove the presence of HAAs in drinking waters, and therefore procedures for HAAs removal are a demanding task.

Currently, treatment alternatives are aimed at the removal of both the precursors and HAAs. Granular activated carbon (GAC) can be employed as an advanced treatment to remove HAAs (Babi et al. 2007; Yang et al. 2010). Although HAA removal is generally ascribed to physical adsorption, biodegradation by the microbial growth in the adsorber bed also occur (Jinkeun and Byeongsoo 2008). Even if biological activated carbon has been recognized more efficient than

autoclaved GAC (Xie and Zhou 2002), some disadvantages, (e.g.: wide pore size distribution, heterogeneous structure, low selectivity), are present (Punyapalakul et al. 2009).

Nanofiltration (NF) is an alternative method for HAAs and precursor control (Koffskey and Lykins 1999; Chellam 2000). Most NF membranes contain charged functional groups and their pore size and membrane surface charge play an important role in solute and water molecules transport across the membrane (Chalatip et al. 2009). In spite of the good removal efficiency achievable, the increase of HAAs concentration in the sample can cause an adverse effect on the performance of NF membranes.

An additional concern of waters on a global scale is the presence of nitrate ion, the stable form of N for oxygenated systems, and naturally occurring ion in the nitrogen cycle.

Its wide occurrence in waters is due to anthropogenic pressures (e.g.: use of fertilizers, urban runoff, landfill leachate, animal manure, erosion of natural deposits, NO<sub>x</sub> air stripping waste from air pollution control devices, *etc.*). Nitrate does not readily bind to the soil causing and is susceptible to leaching. For its high solubility, nitrate is a widespread groundwater contaminant and imposes a serious threat to drinking water supplies, since cause human health problems, particularly for infants. Nitrate contaminated water must be treated properly to meet applicable regulations. Advantages and disadvantages of the main approaches used for nitrate removal (i.e. biological denitrification, zero-valent metals powder, electrodialysis) were recently discussed by Zhu et al. (2006), who propose ultra-filtration for nitrate removal. This procedure requires the addition of quaternary ammonium based-polyelectrolytes to the nitrate solution. Among several treatment technologies, the adsorption with mineral-based and/or surface modified adsorbents has also been explored (Bhatnagar and Sillanpaa 2011).

The aim of this work was the study of the properties of a mesostructured alumino-silicate containing long chain quaternary ammonium ions (cetyltrimethylammonium) as template, i.e. a

precursor of Aluminum containing MCM-41 material (Al-MCM-41), for the removal of HAAs and nitrate in waters.

Sorption behavior of ordered mesoporous silicas has been investigated by current literature with respect to various gas molecules and aqueous ions. Most studies have used materials from which the template had been removed or that may also have been functionalized with ligands specific to certain ions. To the best of our knowledge, in no case MCM-41 materials were employed without functionalization for the removal of inorganic anions in waters. Affinity of surfactant-containing mesostructured silicas (Bruzzoniti et al. 2000) towards TCAA has mainly been ascribed to the surfactant contained inside the mesopores.

In this work we evaluated the potentiality of an Al-containing mesostructured silica for the removal of nitrate and HAAs from waters. Adsorption kinetics and isotherms were also studied.

## **2 Materials and Methods**

### *2.1 Chemicals*

All reagents were from Sigma-Aldrich (Milan, Italy). Aqueous solutions were prepared with high-purity water (Elix-Milli-Q Academic from Millipore, Vimodrone, MI, Italy). Eluents for ion chromatography (IC) were filtered through 0.22  $\mu\text{m}$  filters before use.

### *2.2 Synthesis and characterization of the adsorbent.*

A precursor of Al-MCM-41 was chosen as adsorbent due to the promising performances exhibited (Bonelli et al. 2002). The sample (hereafter denoted as Al-MCM-41-p) was prepared at room temperature starting from a solution of molar composition: TEOS : 0.28 CTABr : 0.017  $\text{Al}(\text{NO}_3)_3$  : 0.6 NaOH : 40  $\text{H}_2\text{O}$ .

After precipitation, the powder was washed with water and dried at room temperature. To achieve a stable surfactant content and to avoid leaching phenomena, the sample was washed in ethanol and then in water until lather was no present.

X-ray diffraction (XRD) analysis was performed on a X'Pert Philips instrument (Cu K<sub>α</sub> radiation). The Al content was evaluated by Electron Dispersive Spectroscopy, EDS (Assing FESEM Supra 25 associated with EDS Oxford Instrument INCA X-Sight), while NMR spectra were obtained with a Bruker Advance II spectrometer, equipped with a magic-angle spin probe using a 4-mm ZrO<sub>2</sub> rotor (internal volume 80 μL).

<sup>27</sup>Al MAS spectrum (104.28 MHz) was measured under experimental conditions of 12.0 kHz spin rate, 0.5 s recycle delay and 1.2 μs pulse. The <sup>27</sup>Al chemical shift scale was referenced to Al(NO<sub>3</sub>)<sub>3</sub> solution (1M).

Thermogravimetric analysis (TG) was performed in air, using a thermal analyzer Setaram-92, in the range between 20 and 800°C, with a heating rate of 10°C/min.

### *2.3 Retention experiments*

0.2 g of the washed Al-MCM41-p were stirred for 45 hours at 25 °C with 10 mL solution containing Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> (ions commonly present in drinking water) and HAAs. Two samples were prepared; sample A: 21 mgL<sup>-1</sup> Cl<sup>-</sup>, 49 mgL<sup>-1</sup> SO<sub>4</sub><sup>2-</sup>, 13 mgL<sup>-1</sup> NO<sub>3</sub><sup>-</sup>; sample B: sample A plus 5 mgL<sup>-1</sup> MCAA, 5 mgL<sup>-1</sup> MBAA, 7.5 mgL<sup>-1</sup> DCAA, 7.5 mgL<sup>-1</sup> DBAA, 25 mgL<sup>-1</sup> TCAA. Sample A was representative of a drinking water sample of our laboratory (Turin, Italy). Triplicate experiments were done and a control was run in parallel. Concentrations of all species were determined by IC.

### *2.4 Chromatographic experiments*

An ion chromatograph ICS3000 (Dionex, Sunnyvale, CA, USA) equipped with a sample loop of 10 μL and a suppressor ASRS-Ultra (Dionex), in external water mode, was used for the determination of inorganic anions and HAAs. All the species were separated simultaneously on a Cryptand Al column, 5 μm, 150 x 3 mm (Dionex), by the following gradient elution: 0 to 3 min 10 mM NaOH;

$t = 3$  min 10 mM LiOH. After the elution of all analytes, a re-equilibration step (8 min) at 10 mM NaOH was set.

### 2.5 Determination of adsorption isotherms

Triplicate batch experiments were carried out. A series of adsorption vessels containing 0.1 g sorbent and MCAA solutions at different concentrations (1, 5, 10, 25, 50 mg/L) was stirred for 45 hours at 25 °C (after verifying that equilibrium conditions were achieved). The same procedure was used for the adsorption study of  $\text{NO}_3^-$ . A control was run in parallel. After filtration of the solution (0.22  $\mu\text{m}$ ), MCAA and  $\text{NO}_3^-$  concentrations were determined by IC.

The amount of MCAA and  $\text{NO}_3^-$  adsorbed at equilibrium ( $q_e$ , mg/g) was calculated by the equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where  $C_0$  is the initial concentration of MCAA or  $\text{NO}_3^-$  solution before adsorption (mg/L),  $C_e$  is the equilibrium concentration of MCAA or  $\text{NO}_3^-$  solution after adsorption (mg/L),  $V$  is the volume of solution (L) and  $m$  is the mass of the sorbent (g).

### 2.6 Determination of adsorption kinetics

Batch kinetics adsorption experiments were carried out stirring 0.1 g of the sorbent with 50 mL solution containing 2.5 mg/L MCAA and 2.5 mg/L  $\text{NO}_3^-$  at 25 °C. Samples were withdrawn regularly at fixed time interval and filtered (0.22  $\mu\text{m}$ ). A control was run and withdrawn in parallel. The filtrates were analyzed by IC to determine residual MCAA and  $\text{NO}_3^-$  concentrations.

## 3 Results and discussion

### 3.1. Physical-chemical characterization of Al-MCM-41-p

The XRD pattern of the sorbent reveals the typical hexagonal symmetry (space group  $p6m$ ) (Meynen et al., 2009). The Al content, as evaluated by means of EDS, is 4% w/w.



The coordination state of Al was evaluated by means of  $^{27}\text{Al}$  MAS NMR. The observed chemical shift reveals that all aluminum atoms are in tetrahedral coordination, indicating that Al was incorporated in the MCM-41 silica framework.

According to the weight loss from the TG analyses in air, the amount of residual surfactant in the sorbent after washing was about 25% w/w.

### 3.2 Retention experiments

#### 3.2.1 Inorganic anions

Our first aim was to check the affinity of the sorbent towards the inorganic anions of drinking water. In order to perform the retention experiments on a matrix matching as much as possible that of drinking water, we determined the composition of a tap water sample ( $21\text{ mgL}^{-1}\text{ Cl}^-$ ,  $49\text{ mgL}^{-1}\text{ SO}_4^{2-}$ ,  $13\text{ mgL}^{-1}\text{ NO}_3^-$ ). Further measurements were performed in a simulated matrix (sample A, § 2.3) of the same composition of the tap water sample analyzed.

The affinity exhibited by Al-MCM-41-p was in the order  $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$ . In detail, the retention percentages were:  $81,7 \pm 0,4\%$  ( $\text{SO}_4^{2-}$ ),  $77,2 \pm 0,4\%$  ( $\text{NO}_3^-$ ) and  $21,4 \pm 0,6\%$  ( $\text{Cl}^-$ ). The sorption obtained for nitrate is definitively higher than those obtained by the use of MCM-41 and MCM-48 modified with  $\text{NH}_2$  groups via co-condensation (removal ranging in a range 20-34%) and post-synthesis grafting (27-36%), (Saad et al., 2008). It should be highlighted that in the afore mentioned case, preliminary acidification of the sorbent was required to convert the amino groups into ammonium moieties which are responsible for the adsorption of anions.

The affinity scale found for Al-MCM-41-p suggests that the sorbent behaves like an anion-exchanger. In fact, the divalent sulfate ion is more retained than the monovalent nitrate and chloride ions, highlighting the contribution of the cationic surfactant, hosted inside the mesostructured silica, to provide fixed charges. The relative high retention exhibited by the Al-MCM-41-p towards nitrate suggests also the contribution of the hydrophobic portion inside the sorbent itself. In agreement

with the hydrophobic nature of the less hydrated nitrate ion, selectivity is enhanced with hydrophobicity of the functional group (Sata et al. 1995).

### *3.2.2 Haloacetic acids*

Further experiments were planned to evaluate the affinity of the sorbent against the regulated HAAs, in the presence of the matrix inorganic anions (fig. 1). HAA5 were added in concentration 800-fold higher than those allowed by EPA (sample B, see § 2.3). Obviously, these concentrations do not respect the composition of drinking water but can represent conditions of sorbent overusing. It was observed that the sorption capacity towards inorganic anions still keeps constant even with a more severe matrix composition (i.e. in the presence of HAA), meaning that there is not a competition effect and that the capacity of the sorbent is not saturated. The retention percentages obtained, 80.1% ( $\text{SO}_4^{2-}$ ), 83 % ( $\text{NO}_3^-$ ) and 23.7% ( $\text{Cl}^-$ ), well compare with the values previously achieved without the presence of HAA. Interesting results were obtained for the regulated HAAs. MCAA was retained in an extent of 20.4%, while for MBAA a 63.8% removal was observed. For DCAA, DBAA and TCAA no peaks were observed in the solution, and hence, based on the quantitation limits of the chromatographic method used (Bruzzoniti, 2008) a removal >99.6% (DBAA), >99,4% (DCAA), >92% (TCAA) was observed, supporting the good retention properties of the sorbent. This result should be considered of high importance, since, although the total concentrations of HAAs vary by seasons, water sources and drinking water treatment plants, the most abundant species are usually TCAA and DCAA making up about 80 % of all HAAs concentrations (Ates et al. 2007; Malliarou et al., 2005).

### *3.2.3 Matrix effect on removal properties*

Further experiments were aimed to check the removal properties of Al-MCM-41-p vs DCAA (7,5 mg/L), DBAA (7,5 mg/L) and TCAA (25 mg/L) with increasing matrix composition. These HAAs were chosen due to their complete adsorption by the sorbent.

Four simulated drinking water samples at increasing chloride, sulphate and nitrate concentrations (Figure 2) were considered. The highest concentration levels (matrix composition D) should be considered precautionary when compared to sample B. In fact, for sulfate, EPA does not provide a Federally enforceable standard, but a guideline, giving a secondary maximum contaminant level of 250 mg/L (US EPA, 2009), based on aesthetic effects (i.e., taste and odor).

No health-based guideline value is proposed for chloride (WHO, 2003), but concentrations higher than 250 mg/L can give rise to detectable taste. River-, lake- and groundwaters usually contains chloride at concentrations well below 250 mg/l, while high concentrations are expected for aquifers prone to seawater intrusion (Marandi and Karro 2008). For nitrate EPA sets 10 mg/L as maximum contaminant level (US EPA, 2011).

As far as Italian regulation for drinking water is concerned (Italian legislative decree, 2001), 50 mg/L and 250 mg/L are set for nitrate and chloride, respectively.

As shown in fig. 2, for concentrations as high as 50 ppm chloride, 50 ppm sulphate and 10 ppm nitrate, removal of HAAs is included within 12.5% (DCAA) and 72 % (TCAA). The removal performance of the sorbent keeps constant and particularly high for TCAA, even increasing matrix concentration up to 100 ppm chloride, 100 ppm sulphate and 30 ppm nitrate. The adsorption capacity (TCAA>DBAA>DCAA) reflects the retention order obtained in IC separations (Bruzzoniti et al. 2008), thus supporting that an ion-exchange mechanism is acting.

#### *3.2.4 Recovery of pollutants from Al-MCM-41-p*

For a possible regeneration of the material, washing procedures were also investigated. Based on the mechanisms hypothesized (ion-exchange and hydrophobic interaction), NaOH and methanol were chosen as suitable solvents.

The sorbent was preliminarily loaded with sample B and subsequently treated with 10 mL 1 mM NaOH and then with 10 mL 1:1 (v/v) H<sub>2</sub>O-CH<sub>3</sub>OH. While NaOH removes quantitatively the chloride ions sorbed, recoveries for sulfate and nitrate were 8.2% and 11% respectively. Water-

methanol solution, reducing the analyte-sorbent hydrophobic interactions, removed nitrate quantitatively and DCAA (66%) and DBAA (53%), but it is not effective in recovering TCAA. The washing procedure recovered 0.61 mg pollutants of the 1.33 mg initially sorbed (about 46%).

### 3.3 Adsorption isotherms

The adsorption isotherms were determined for two probes, one inorganic (nitrate) and the other organic, among those which not exhibited quantitative retention (MCAA or MBAA). MCAA was definitively chosen for its higher occurrence frequency in the distribution systems (Golfinopoulos and Nikolaou 2005). The adsorption isotherms are shown in fig. 3. For both the analytes, for concentrations as high as 50 mg/L, the sorbed amount is about 2.5 mg/g. With the purpose to model the adsorption, three isotherm models were used to test experimental data (Langmuir, Freundlich and Temkin).

Langmuir adsorption isotherm is often applied in solid/liquid systems to describe the saturated monolayer adsorption. The formation of a monolayer of adsorbate on the outer surface of the adsorbent is assumed. A linear form of the Langmuir equation is given by

$$\frac{C_e}{q_e} = \frac{1}{k_L x_{monolayer}} + \frac{C_e}{x_{monolayer}} \quad (2)$$

The intercept and the slope of the plot allow to calculate  $k_L$  (the adsorption equilibrium constant, L/mg) and  $x_{monolayer}$  (the monolayer's adsorption capacity, mg/g).

The dependence of  $C_e/q_e$  on  $C_e$  is not linear in the whole range of  $C_e$ , for both the species ( $r^2_{MCAA}=0.4180$ ;  $r^2_{nitrate}=0.0065$ ).

The Freundlich adsorption isotherm, based on adsorption model on heterogeneous surface, is an empirical equation to describe multilayer adsorption at energetically heterogeneous surface and can be written as

$$q_e = KC_e^n \quad (3)$$

Where  $K$  is the adsorption coefficient and  $n$  is a measure of deviation of isotherm from the linear form, i.e. the heterogeneity factor. The dependence of  $\ln q_e$  on  $\ln C_e$  is linear and well explain adsorption of MCAA ( $r^2_{\text{MCAA}}=0.9786$ ) and nitrate ( $r^2_{\text{nitrate}}=0.9709$ ). The values of  $K$  and  $n$  are calculated from the intercept and the slope of the plot. For MCAA,  $K$  ( $\text{mg}^{1-1/n} \text{ L}^{1/n} / \text{g}$ ) = 0.127,  $n=1.069$ ,  $R^2=0.9786$ , while for  $\text{NO}_3^-$ ,  $K$  ( $\text{mg}^{1-1/n} \text{ L}^{1/n} / \text{g}$ ) = 0.0952,  $n=0.942$ ,  $R^2=0.9709$ . Since, for both the species,  $1/n \sim 1$ , a linear adsorption and, therefore, equal adsorption energies for all sites can be hypothesized (Delle Site 2001).

Interestingly, the values of  $K$  and  $n$  are in agreement with those obtained by Punyapalakul et al. (2009) for mesoporous silica modified with amino functional groups, who reported the values  $K=0.158$  and  $n=1.104$  for DCAA as well as a higher correlation with Freundlich isotherm, rather than with the Langmuir model.

The Temkin model, finally evaluated, postulates that the heat of adsorption varies linearly with coverage, unlike the Freundlich method, in which a more complex dependence of the heat of adsorption on the coverage is assumed (i.e. the heat of adsorption decreases exponentially with increasing coverage) (Lowell et al. 2004) and can be expressed as:

$$q_e = a + b \ln C_e \quad (4)$$

Where  $a$  and  $b$  are Temkin constants.

As in the case of Langmuir model, the dependence of  $q_e$  vs  $\ln C_e$  is not linear in the whole range of  $C_e$  ( $r^2_{\text{MCAA}}=0.8047$ ;  $r^2_{\text{nitrate}}=0.8743$ ).

### 3.3 Adsorption kinetics

The adsorption kinetics profile for MCAA and nitrate is reported in Fig. 4. Concentrations of both species decrease rapidly in the first 10 min. Experiments performed after 45h (data not included) showed same values measured after 1h, indicating that the equilibrium was reached after 1 h.

In order to investigate the mechanism of sorption and potential rate controlling steps such as mass transport and chemical reaction processes, pseudo-first order (Ho 2004), pseudo-second order (Ho 1994) and Elovich (Low 1960) kinetics models were used to test experimental data.

The first may be written as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

Where  $q_t$  is the amount (mg/g) of MCAA or  $\text{NO}_3^-$  sorbed at time  $t$ , and  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant of pseudo-first order. In order to fit eq. (5), the value of  $q_e$  must be assigned (Ho 1998); in this approach we used the value obtained by experimental measurements after 45h adsorption.

The slope and intercepts of the  $\ln(q_e - q_t)$  vs  $t$  plots were used to determine the rate constant  $k_1$ . The results (table 1) show a fair relationship with the model ( $r^2_{\text{MCAA}}=0.9817$ ;  $r^2_{\text{nitrate}}=0.9318$ ).

The pseudo-second order model may be expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

Where  $k_2$  ( $\text{mg g}^{-1} \text{min}^{-1}$ ) is the rate constant of pseudo-second order adsorption. The slope and intercepts of the  $t/q_t$  vs  $t$  plots were used to determine the rate constant and the adsorption capacity.

As shown in table 1, an excellent agreement with the experimental results was obtained ( $r^2 > 0.999$ ) as well as a very good consistency of the calculated  $q_e$  value with the experimental data.

The Elovich equation, having general application to chemisorption kinetics, was also used. This equation has been applied satisfactorily to some chemisorption data and has been found to cover a large range of slow adsorption (Cheung et al. 2000). The Elovich equation is often valid for systems in which the adsorbing surface is heterogeneous. In the simplified form, it can be written as

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (7)$$

Where  $\alpha$  is the initial sorption rate ( $\text{mg g}^{-1} \text{min}^{-1}$ ) and  $\beta$  is the desorption constant ( $\text{g mg}^{-1}$ ) during an experiment.

Despite the good correlations ( $r^2_{\text{MCAA}}=0.9395$ ;  $r^2_{\text{nitrate}}=0.9718$ ), table 1, the pseudo-second order model provided the best fitting of the experimental data.

Many researchers found that if a reaction is controlled by ion-exchange, the pseudo-second order model has best fit with experimental data (Lei et al. 2008; Zheng et al. 2008; Zhu et al. 2011). Hence, the above results together with the retention affinity data obtained (§3.2.2 and §3.2.3) are in agreement with an ion-exchange mechanism acting between the sorbent and the species.

## **Conclusions**

The retention properties of a Al-MCM-41 precursor towards the five regulated HAAs in a simulated drinking water sample were studied, as well as the removal characteristics in the presence of increasing concentrations of matrix components ( $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ).

The sorbent has the following affinity:  $\text{TCAA}=\text{DBAA}=\text{DCAA}>\text{MBAA}>\text{MCAA}$  and it is able to completely remove DCAA, DBAA and TCAA. High removal has been also achieved for nitrate.

Adsorption kinetics and isotherms studies were also performed. The adsorption isotherms of  $\text{NO}_3^-$  and MCAA can be both modeled by the Freundlich equation, while their adsorption kinetics follow a pseudo-second order rate mechanism, in agreement with an ion-exchange mechanism.

The recovery of pollutants from the sorbent was finally investigated, proving that nitrate can be completely removed. This characteristic, as well as the good retention results obtained for nitrate, suggest that the material can be applied to develop technologies for environmental remediation of pollution in natural waters.

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## **Supplementary Material**

XRD pattern, <sup>27</sup>Al MAS NMR spectrum and TG analyses for sorbent characterization are available, as well as application of linearized adsorption isotherms and kinetics.



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## Figure Captions

**Fig. 1.** Sorption of the regulated HAAs from a simulated drinking water matrix (21 mg/L chloride, 49 mg/L sulfate, 13 mg/L nitrate).

**Fig. 2.** Effect of matrix composition on the removal of DCAA (7.5 mg/L), DBAA (7.5 mg/L) and TCAA (25 mg/L). Matrix composition: A: 25 mg/L  $\text{Cl}^-$ , 25 mg/L  $\text{SO}_4^{2-}$ , 5 mg/L  $\text{NO}_3^-$ ; B: 50 mg/L  $\text{Cl}^-$ , 50 mg/L  $\text{SO}_4^{2-}$ , 10 mg/L  $\text{NO}_3^-$ ; C: 70 mg/L  $\text{Cl}^-$ , 70 mg/L  $\text{SO}_4^{2-}$ , 20 mg/L  $\text{NO}_3^-$ ; D: 100 mg/L  $\text{Cl}^-$ , 100 mg/L  $\text{SO}_4^{2-}$ , 30 mg/L  $\text{NO}_3^-$ .

**Fig. 3.** MCAA and nitrate adsorption isotherms. Initial concentrations from 1 to 50 mg/L, adsorbent loading (0.1 g/10 mL).

**Fig. 4.** MCAA and nitrate adsorption kinetics. Concentrations of both species 2.5 mg/L, adsorbent loading (0.1 g/50 mL).

## Table Captions

**Table 1.** Adsorption isotherm constants for the three kinetics models evaluated.

**Table 1.** Adsorption isotherm constants for the three kinetics models evaluated.

	Pseudo-first order		Pseudo-second order				Elovich			
	$k_1$ ( $\text{min}^{-1}$ )	$R^2$	$K_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	Calculated $q_e$ ( $\text{mg g}^{-1}$ )	Experimental $q_e$ ( $\text{mg g}^{-1}$ )	$h^a$ ( $\text{mg g}^{-1} \text{min}^{-1}$ )	$R^2$	$\alpha$ ( $\text{mg g}^{-1} \text{min}^{-1}$ )	$\beta$ ( $\text{g mg}^{-1}$ )	$R^2$
MCAA	0.0283	0.9817	16.28	0.0956	0.0978	0.149	0.9994	$6.05 \cdot 10^{10}$	370.4	0.9395
Nitrate	0.0622	0.9318	12.46	0.1022	0.1013	0.130	0.9996	$1.08 \cdot 10^4$	181.8	0.9718

<sup>a)</sup> initial adsorption rate calculated from  $h=k_2q_e^2$ .

## Figures

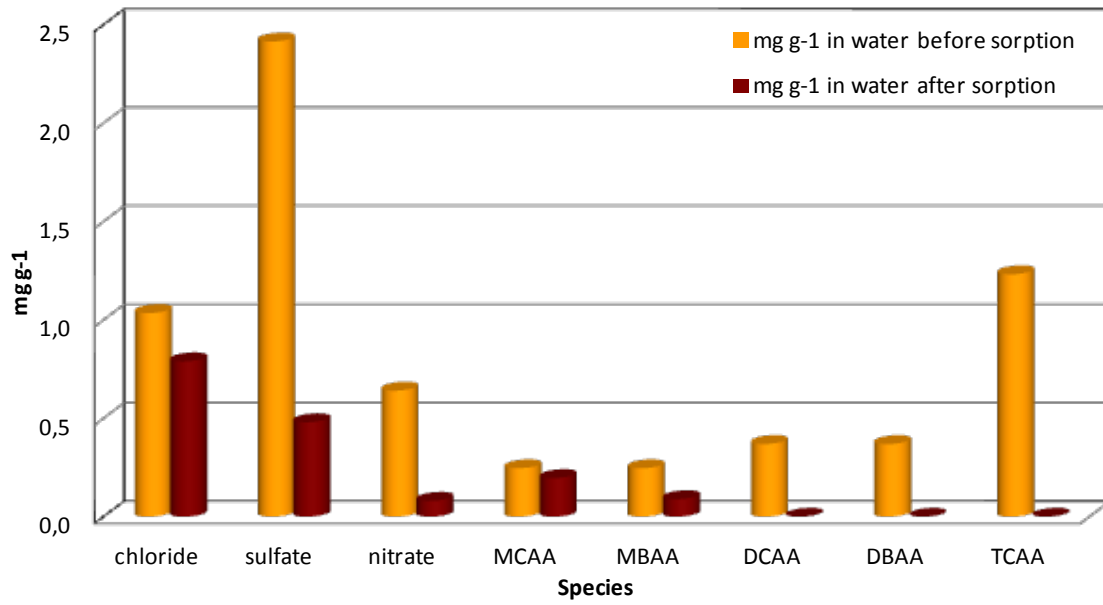


Fig. 1.  
Sorption of the regulated HAAs from a simulated drinking water matrix (21 mg/L chloride, 49 mg/L sulfate, 13 mg/L nitrate). Other experimental details in section 2.3.



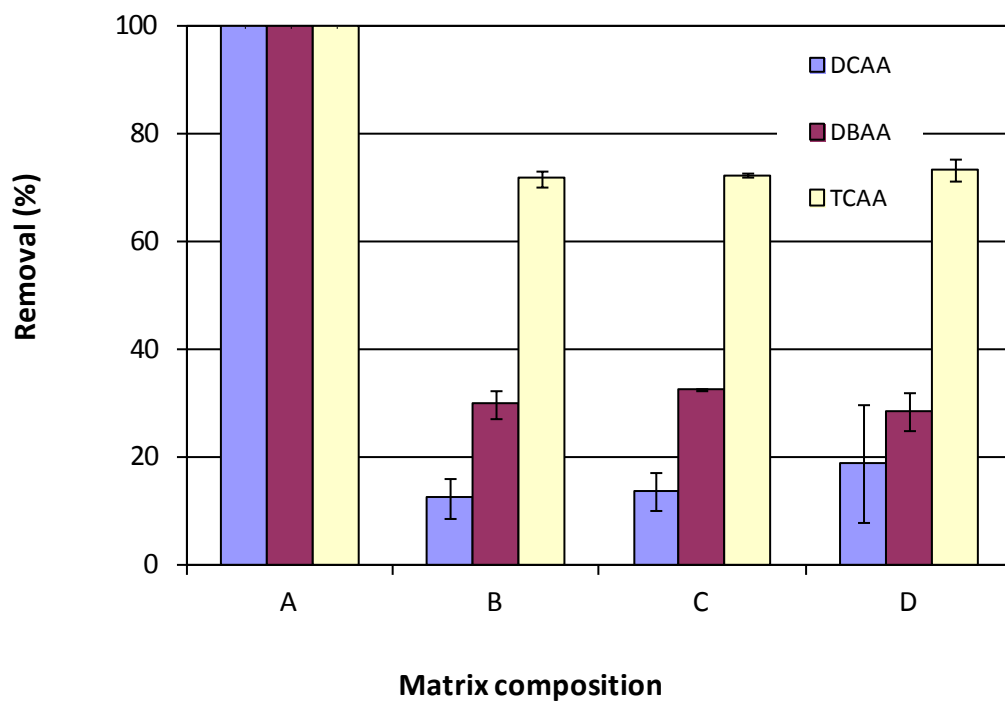


Fig. 2. Effect of matrix composition on the removal of DCAA (7.5 mg/L), DBAA (7.5 mg/L) and TCAA (25 mg/L). Matrix composition: A: 25 mg/L  $\text{Cl}^-$ , 25 mg/L  $\text{SO}_4^{2-}$ , 5 mg/L  $\text{NO}_3^-$ ; B: 50 mg/L  $\text{Cl}^-$ , 50 mg/L  $\text{SO}_4^{2-}$ , 10 mg/L  $\text{NO}_3^-$ ; C: 70 mg/L  $\text{Cl}^-$ , 70 mg/L  $\text{SO}_4^{2-}$ , 20 mg/L  $\text{NO}_3^-$ ; D: 100 mg/L  $\text{Cl}^-$ , 100 mg/L  $\text{SO}_4^{2-}$ , 30 mg/L  $\text{NO}_3^-$ .

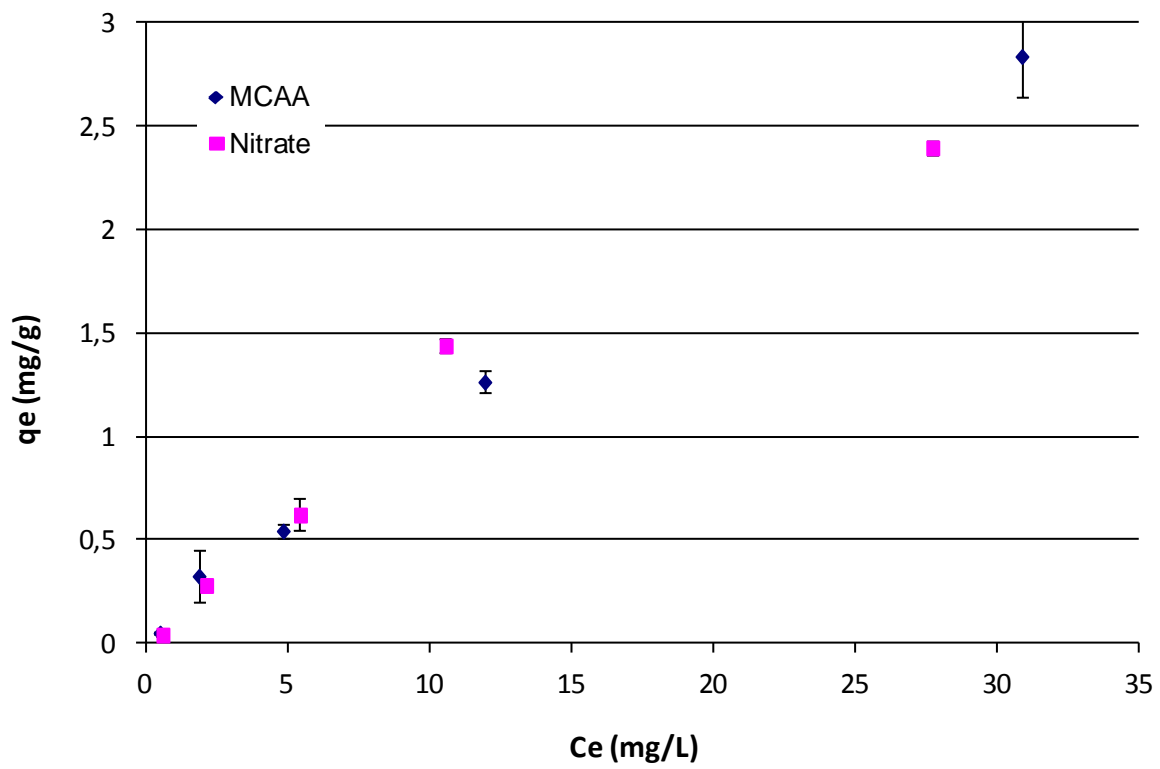


Fig. 3. MCAA and nitrate adsorption isotherms. Initial concentrations from 1 to 50 mg/L, adsorbent loading (0.1 g/10 mL).

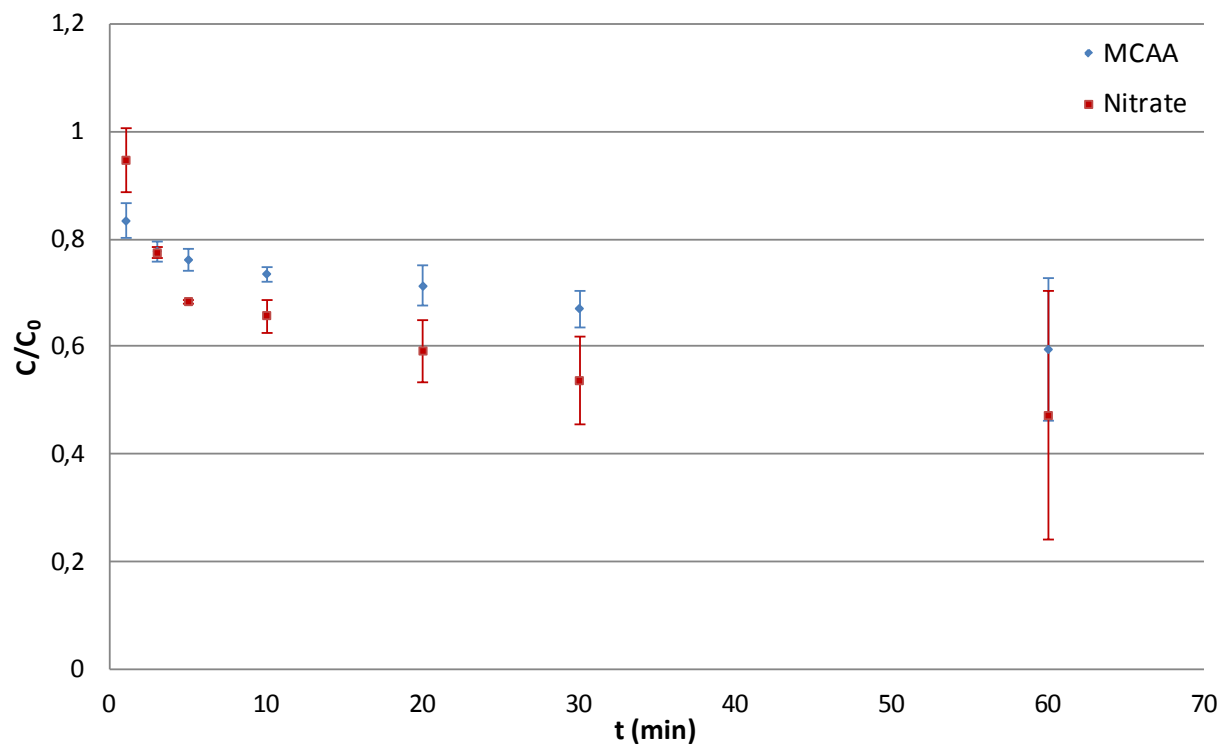
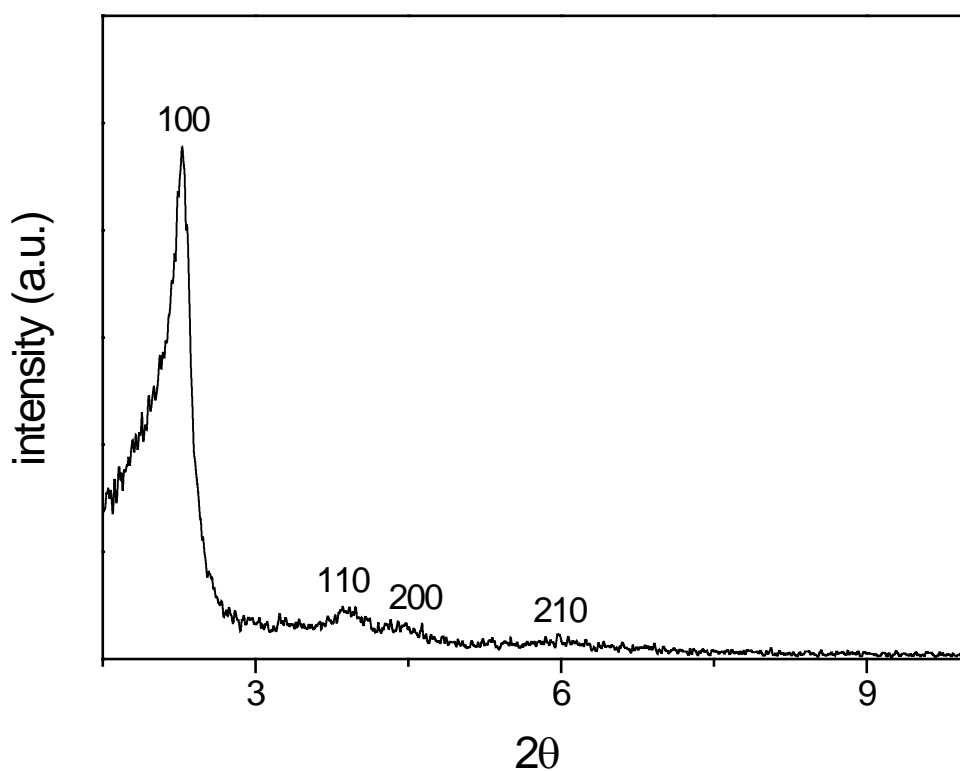


Fig 4  
MCAA and nitrate adsorption kinetics. Concentrations of both species 2.5 mg/L, adsorbent loading (0.1 g/50 mL).

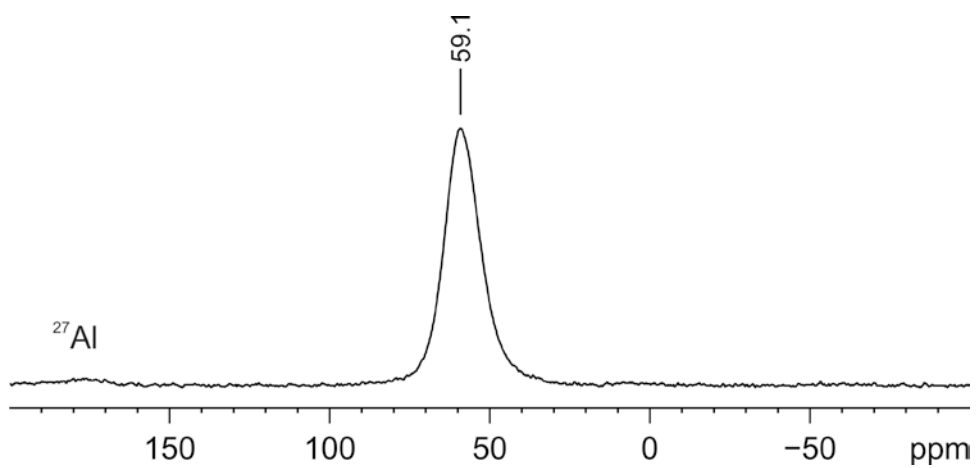
# Novel insights in Al-MCM-41 precursor as adsorbent for regulated haloacetic acids and nitrate from waters

Maria Concetta Bruzzoniti, Rosa Maria De Carlo, Corrado Sarzanini, Dario Caldarola, Barbara Onida

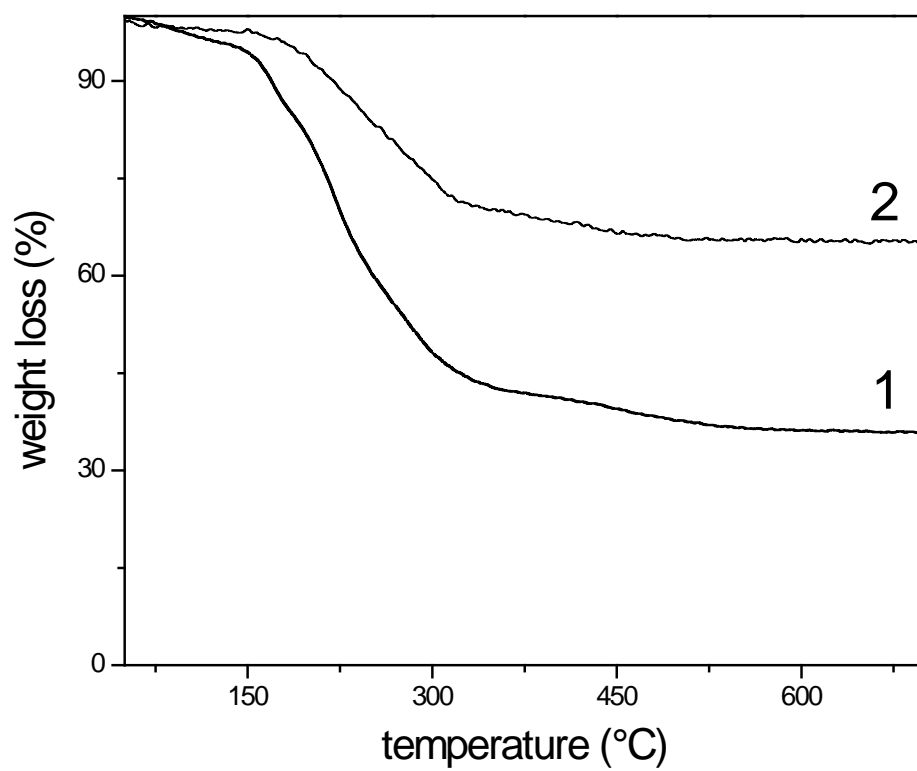
## Supplementary Material



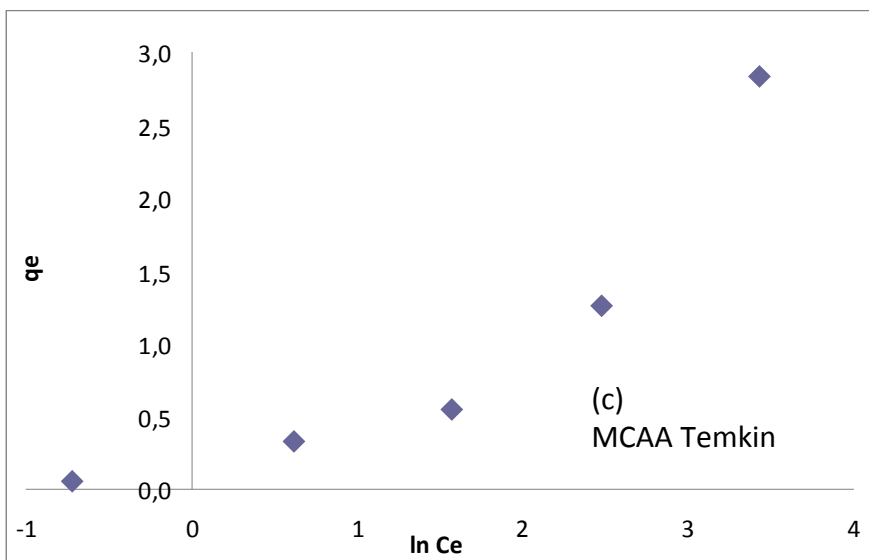
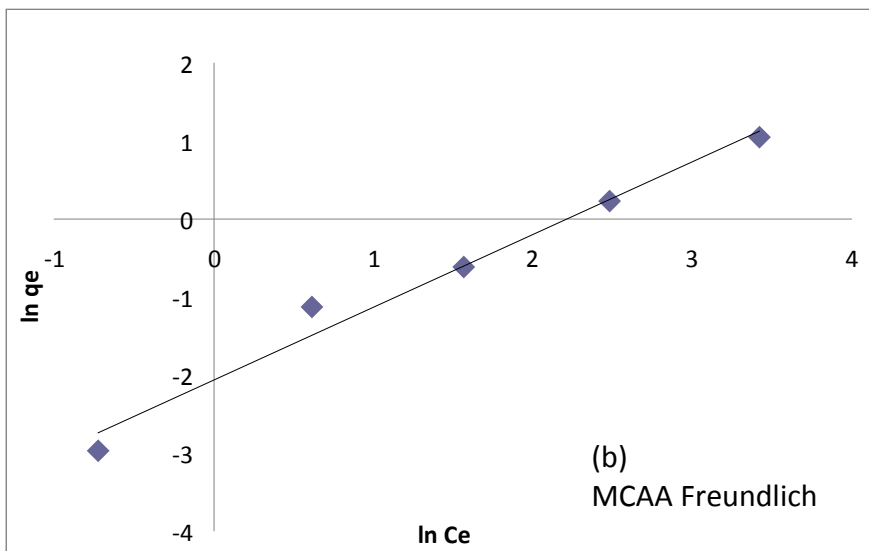
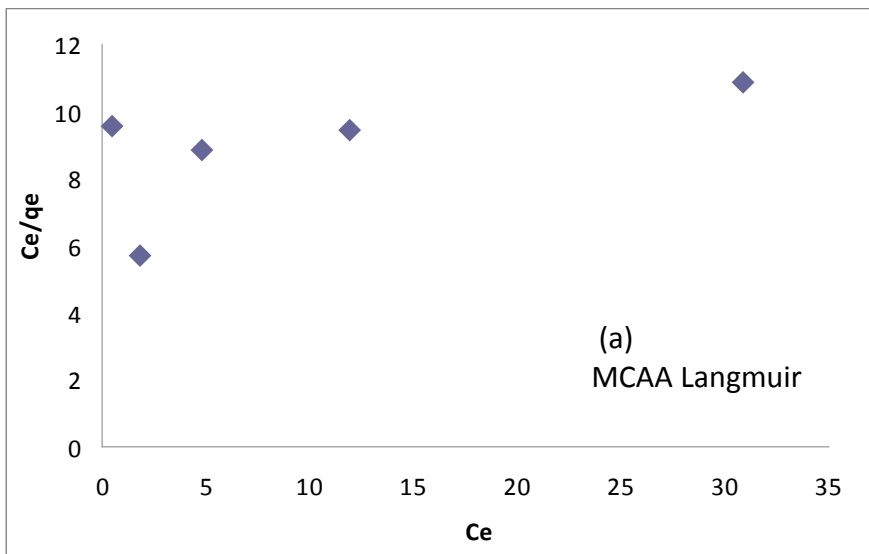
XRD pattern of Al-MCM-41-p with indexed reflections.



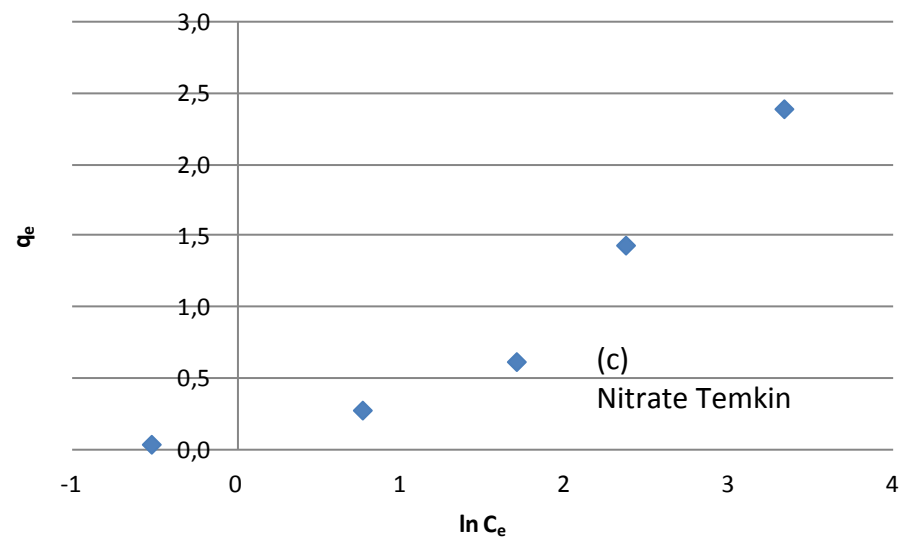
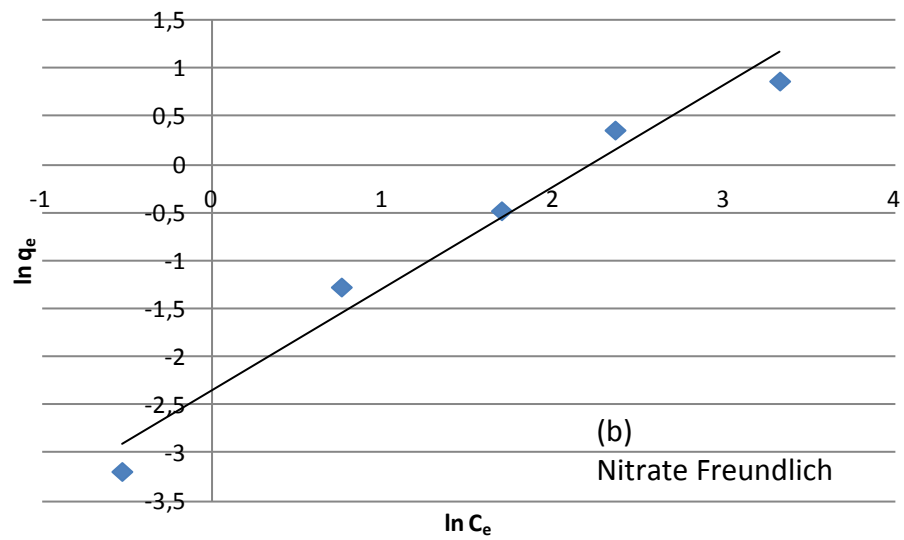
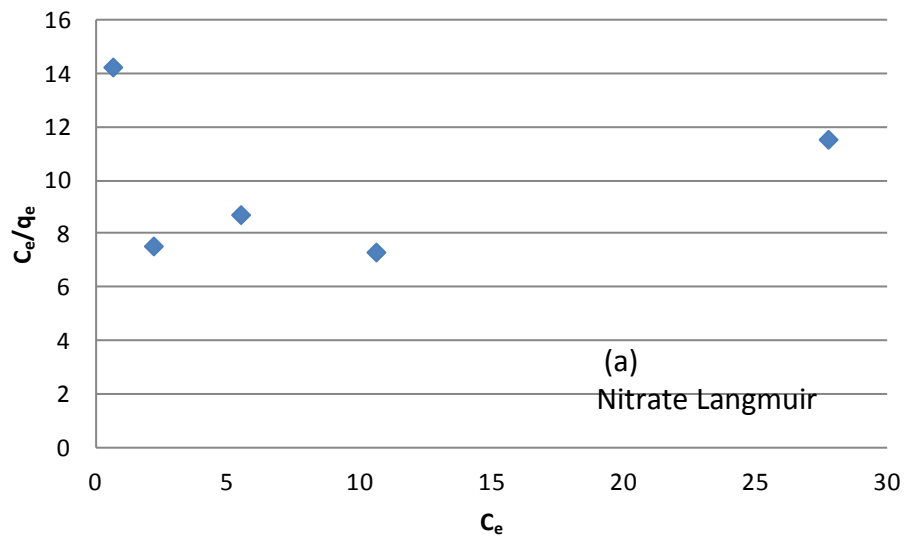
$^{27}\text{Al}$  MAS NMR spectrum of Al-MCM-41-p.



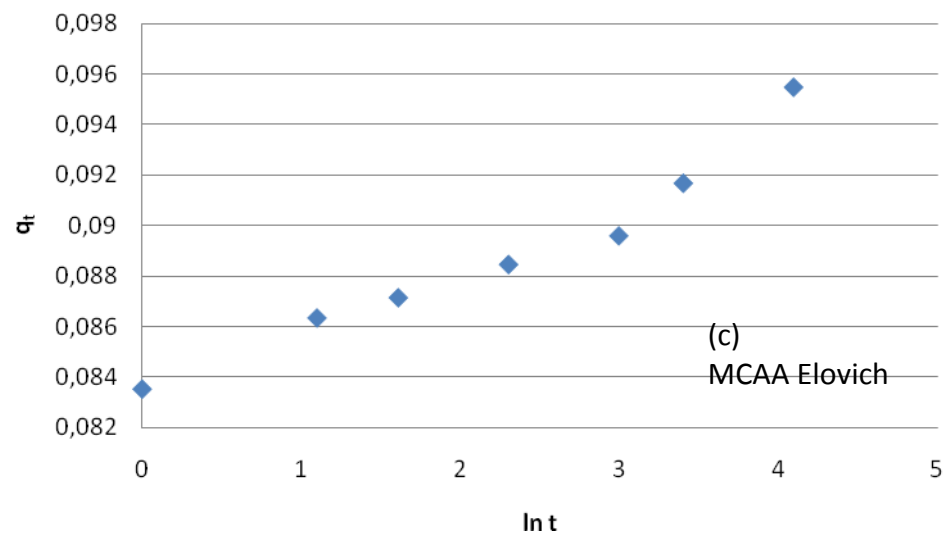
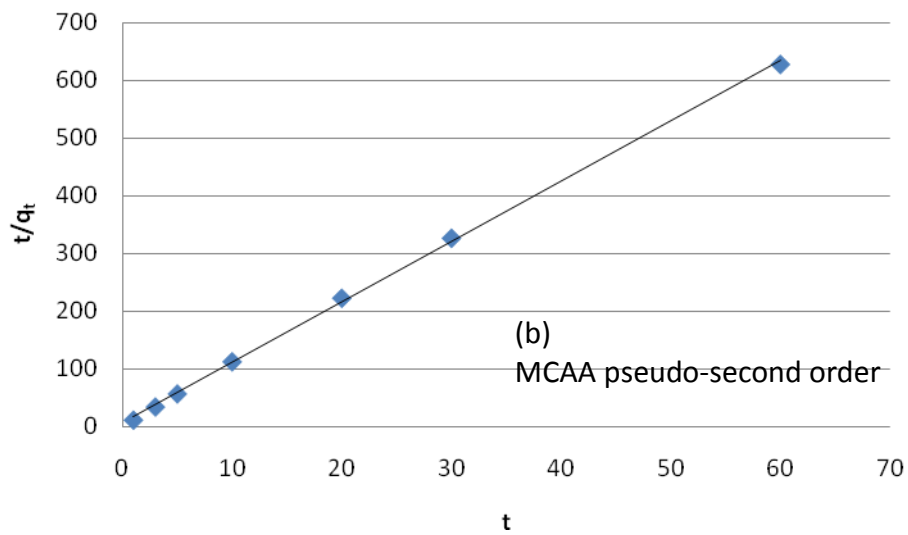
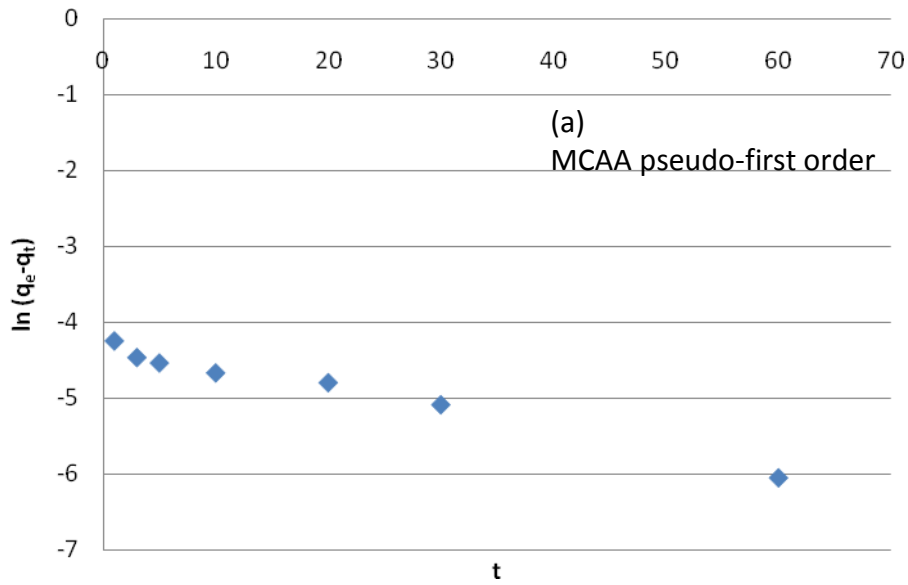
TG analysis of Al-MCM-41-p before (curve 1) and after (curve 2) washing.



Application of linearized Langmuir (a), Freundlich (b) and Temkin (c) models to experimentally obtained isotherms for MCAA.

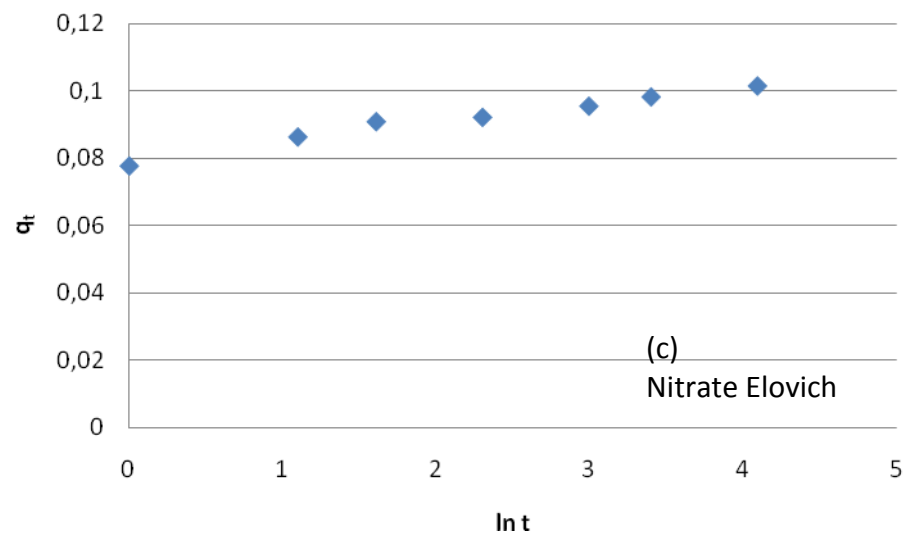
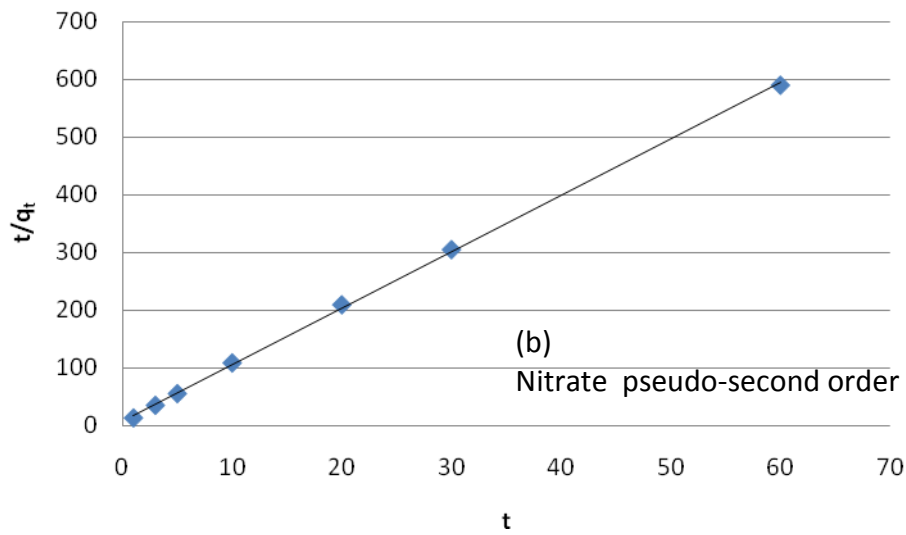
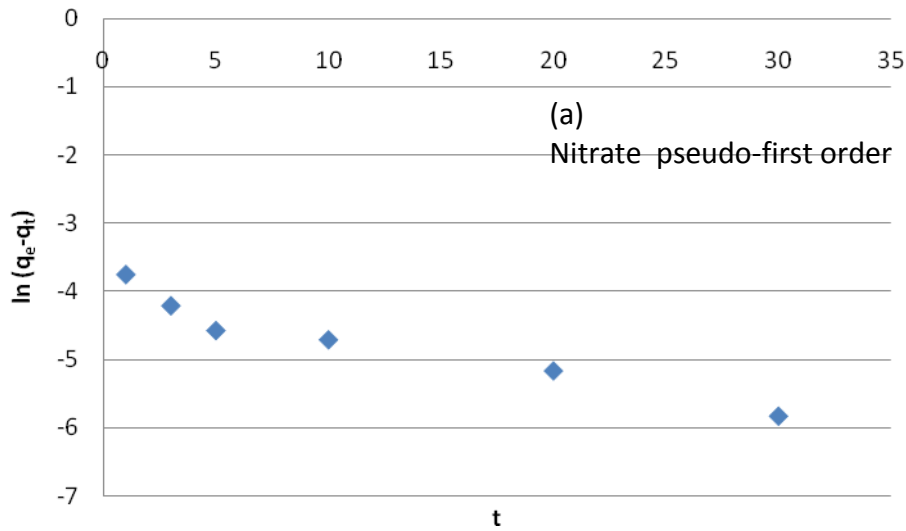


Application of linearized Langmuir (a), Freundlich (b) and Temkin (c) models to experimentally obtained isotherms for nitrate.



Application of different kinetics models to experimentally obtained data for MCAA. Pseudo-first order (a), pseudo-second order (b) and Elovich (c) models.





Application of different kinetics models to experimentally obtained data for nitrate. Pseudo-first order (a), pseudo-second order (b) and Elovich (c) models.