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Adsorption of phenol from aqueous solution onto Faujasite zeolites with different Si/Al ratios

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ABSTRACT/RESUME

Abstract: *Adsorption of phenolfrom aqueous solution onto zeolites has been investigatedin the region of low concentrations (10 to 100 mg L^{-1}).Materials used are zeolites Y (Faujasite structure) with different Si/Al ratio (5.2, 30 and 60) in order to determine the effect of Al content on organic molecules uptake. Results show that capacity of adsorption increases with Si/Al ratio, indicating that for selective adsorption of phenol from aqueous solution adsorbent must be hydrophobic, which implies low aluminum content in the zeolite structure. Experimental data were fitted by the models of Langmuir, Freundlich and Dubinin-Raduskevich calculated by non-linear regression, in order to determine adsorption parameters, which showed us that on the more silicic zeolite the competition effect of water molecules to occupy the active surface is lower.*

I. Introduction

Pollution of water and groundwater by organic molecules none biologically degradable is one of cause of environment deterioration. Adsorption techniques are extensively used for elimination of such pollution. Activated carbons are the most widely used in this field, due to their high surface area and hydrophobic character, but the disadvantage of such materials is their high regeneration cost, increasing the request to find other efficient materials easily regenerable [1, 2].

Zeolites, which are inorganic crystalline materials, can constitute an alternative for activated carbon, since these solids have a great capacity of adsorption. They can be modified easily and can be regenerated by oxidation under air. Natural zeolites are very attractive materials since they are not expensive and available. Many investigations were carried out on this type of materials, for an eventual application as adsorbents [3-7]. However, they are hydrophilic due to their high content on aluminum and other minerals (Ca, Mg, K, Na...) witch have à high affinity for water molecules. In addition, they offer limited possibilities in term of pore size. Synthetic zeolites are more interesting because they offer more options in term of pores size, Si/Al ratio and they canbe easily tailored. Indeed, there is many works dealing with use of synthetic zeolites in adsorption of different water contaminants [8-14].

Zeolite Y, which possesses Faujasite structure (FAU), is largely employed in catalysis industry particularly for gasoline production. This three-dimensional framework structure is much ventilated, with cavities in form of cages having large openings (7.4 Å). Okolo et al. [15], studied adsorption of phenol and chlorophenol by zeolite Y (FAU) and activated carbon. They found that activated carbon was more efficient due to its superior hydrophobicity. Roostaei et al. [16] in their study, rapport that zeolite FAU had higher adsorption capacity than MFI of Si/Al ratio of ∞. Koubassy et al. [17], studied the adsorption of nitrophenols (NP) by three structures: BEA (Si/Al ∞), MFI (Si/Al = 500) and FAU (Si/Al = 100). They found that zeolite BEA has the highest adsorption capacity, due to its more hydrophobic character but adsorption capacity of FAU is higher than that of MFI despite being more hydrophobic but it has smaller pore opening. Khalid et al. [18], studied the effect of structure on adsorption capacity of phenol in a concentration interval varying from 0.1 to 1.6 g L^{-1}. They found that for the same Si/Al ratio Faujasite structure is more effective than BEA and Mordenite which have comparable pore size. Braschi et al. [19] Martucci et al. [20], made the same observations inadsoption of pharmaceuticals from aqueous solution by different eolitic structures with the same Si/Al ratio. They found that FAU structure has the highest adsorption capacity compared to MFI and MOR.

Precedent studies had clary shown that the main parameters affecting adsorption of organic compounds in aqueous solution are zeolites pores openings and hydrophobicity. The aim of this work is to study adsorption of phenol from aqueous solution onto FAU zeolite structure with different Si/Al ratio, on region of low concentrations, in order to have a better understanding on affinity and adsorption behavior of organic molecules and consequently depollution proprieties of this type of zeolitic structure.

II. Experimental

II.1. Materials

All reagents used in this study are of analytical grade. Zeolites are in protonic form supplied by Zeolyst International (characteristics are listed in Table 1). The pollutant used is phenol (99% Aldrich, Germany), solutions were prepared using distillated water. The zeolites were placed in drying oven at 105 °C to remove physisorbed water before their use

II.2. Characterization methods

Porosity was probed by physiorption of nitrogen at 77 K by a gas adsorption system ASAP 2000 (Micromeritics). The specific area was determined by the Brunauer–Emmett–Teller approach using 0.10 as the maximum value of relative pressure. Microporous volume was determined by the Dubinin-Raduskevich (D-R) equation and external surface area was obtained by the t-plot method. Zeolite structure was characterized by powder XRD analysis with an X Pert Pro Panalyticaldiffractometer using Cu Kα_1 radiation over the range (2θ) of 0-80°.

II.3. Adsorption experiments

Adsorption was carried out at room temperature under atmospheric pressure, using batch conditions. It was performed by introducing a mass of zeolite into a glass Erlenmeyer of 100 ml, containing 50 ml of an aqueous solution of phenol of determined concentration. The mixture was stirred with a magnetic agitation at 150 rpm for the desired period. Then, the separation was performed by centrifugation at 6000 rpm during 5 min and the suspension was analyzed by UV-Visible spectroscopy at wavelength of 270 nm to determine the residual concentration of phenol.

The amount of phenol adsorbed by the adsorbateq_{ads} (mg g^{-1}) was calculated according to:

$$q_{ads} = \frac{V}{m}(C_0 - C_e)$$

where$V$ is the volume of the solution (L), C_0 the initial concentration (mg L^{-1}), C_e the equilibrium concentration (mg L^{-1}), and m is the weight of the adsorbent (g).

The adsorption percentage is calculated according to:

$$\% = \frac{C_0 - C_e}{C_0} \times 100$$

II.4. Adsorption isotherms

The adsorption equilibrium was evaluated by the models of Langmuir, Freundlich and Dubinin-Raduskevich (D-R). Parameters of each model were calculated by non-linear fitting using Origin 6.0 software.

The simplest model for adsorption corresponds to the Langmuir isotherm which is used to describe adsorption by homogenous surface is given by:

$$q_{\mathrm{ads}} = q_{\mathrm{max}} \frac{b\, C_{\mathrm{e}}}{1 + bC_{\mathrm{e}}}$$

whereq_{ads} is the quantity adsorbed per gram of solid at the equilibrium (mg g^{-1}), q_{max} is the saturation capacity (mg g^{-1}), C_{e} (mg L^{-1}) the equilibrium concentration of the adsorbate and b is the affinity constant or Langmuir constant (L mg^{-1}) [21].

Another simple equation for representing adsorption data is the Freundlich isotherm used to describe adsorption by heterogeneous surface:

$$q_{ads} = K_F C_e^{1/n}$$

where K_F is a constant indicative of the adsorption capacity of the adsorbent and n is an empirical constant called the Freundlich coefficient [22].

The model of Dubinin-Raduskevich (D-R) is used to estimate the apparent free energy of adsorption as well as to make a distinction between physical and chemical adsorption process. The D–R equation was given by the following relationship:

$$q_{ads} = q_{max}\exp(-\beta\varepsilon^2)$$

whereq_{max} is the theoretical saturation capacity, β is the activity coefficient related to mean sorption energy and ε is the Polanyi potential given by:

$$\varepsilon = RT\, \mathrm{Ln}\, (C_s/C_e)$$

where C_s (mg L^{-1}) is solubility of the solute.

The D–R constant β can give the valuable information regarding the mean energy of adsorption (E) by the following equation:

$$E = (2\beta)^{-1/2}$$

the magnitude of E gives the information about the type of adsorption process: physical (1-8 kJ mol^{-1}), ion exchange (9–16 kJ mol^{-1}) and chemical (>16 kJ mol^{-1}) [23, 24].

III. Results and discussion

III.1. Characterization

Results of nitrogen adsorption measurements are given in *Table 1*. These results indicate presence of considerable mesoporousfraction, which increases with the Si/Al ratio, probably caused by post-synthesis treatments of dealumination, usually performed to increase Si/Al ratio and which causes textural modifications. The same tendency is followed by the microporous volume for the same raison. External surface is very smaller than total surface; therefore, only small portion of adsorption surface is easily accessible and majority of adsorption sites are located inside crystallites. Therefore, these zeolites have a greater effectiveness for adsorption of the molecules with kinetic diameter lower than pores openings (<7.4 Å). XRD analysis shows the same patterns for the three zeolites which are characteristic of Faujasite structure and no other crystalline phase is observed.

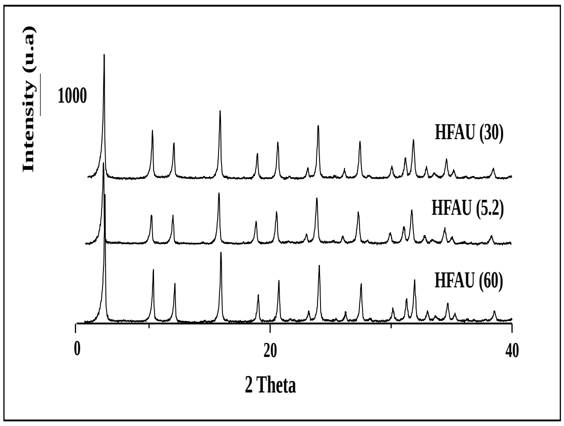


Figure 1. *The XRD patterns of the zeolites.*

III.2. Effect of the Si/Al ratio on the percentage of adsorption

The study of the influence of Si/Al ratio is carried out in order to highlight the effect of the hydrophobic character of the zeolite onto adsorption capacity, which is related to the aluminum content of zeolite. *Figure 2 and Table 2* show that the capacity of adsorption increase with Si/Al ratio. This increase in adsorption percentage (and adsorption capacity) is attributed to the increase in the hydrophobic character of zeolites, related to diminution of Al content responsible for increasing affinity of the adsorbent for water. Consequently, when the amount of Al of the zeolite (framework and extra-framework) is reduced, there is a reduction of competition between water and phenol molecules for the occupation of the active surface.

Influence of experimental parameters have been conducted only for HFAU (60) which possess the highest adsorption capacity, due to its higher hydrophobic character since it have the lowest amount of Al (framework and extra-framework).

III.3. Adsorption kinetic

The effect of the contact time is carried out with aim of determining the equilibrium time. As we can see from *Figure 3*, adsorption of phenol is very fast and equilibrium is reached after the first minute. This result is obvious since phenol molecules possess a kinetic diameter of 0.6 nm, which is lower than pore size of FAU zeolite (0.74 nm) and evidently penetrates easily inside the crystallites. Thus, there is no diffusional limitation (intra and inter-particular diffusion) for phenol and other molecules with comparable size and adsorption can occur as well inside or outside zeolite crystal. Hence, such fast adsorption is very desirable in depollution process, since it allows considerable time-saver.

III.4.Effect of pH on adsorption equilibrium

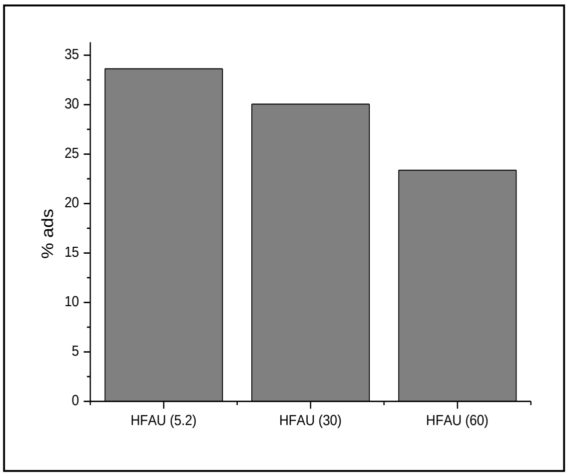
Study of the impact of the pH on adsorption balance was carried out for values ranging between 3 and 11, on which the zeolite structure is notdeteriorated. The pH is adjusted by solutions ofNaOH and HCl 0.1 M. From *Figure 4* we see that thepH does not affect adsorption went it is between 3 and 9. However, an important decrease is observed when pH is higher than 9. This diminution is causedby the increase of phenolates concentration resulting from phenol dissociation, which is more pronounced at basic values of pH. These phenolates are pushed back by the negatively charged zeolite framework.

Table 1. *Textural proprieties of the adsorbent.*

Zeolite	S_{BET} (m^2 g^{-1})	S_{ext}(m^2 g^{-1})	V_t (cm^3 g^{-1})	V_{mic} (cm^3 g^{-1})	V_{mes} (cm^3 g^{-1})
HFAU (5.2)	670	99	0.374	0.265	0.109
HFAU (30)	907	119	0.507	0.364	0.142
HFAU (60)	946	123	0.535	0.383	0.152

Table 2. *Effect of Si/Al ration on the adsorption capacity.*

Zeolite	Si/Al	Formula	n_{Al} (mmolg^{-1})	% ads	q_{ads} (mg g^{-1})
HFAU(60)	60	$H_3Al_3Si_{189}O_{384}$	7.03	33.62	0.89
HFAU(30)	30	$H_6Al_6Si_{186}O_{384}$	14.06	30.05	0.79
HFAU (5.2)	5.2	$H_{31}Al_{31}Si_{161}O_{384}$	72.65	23.37	0.62



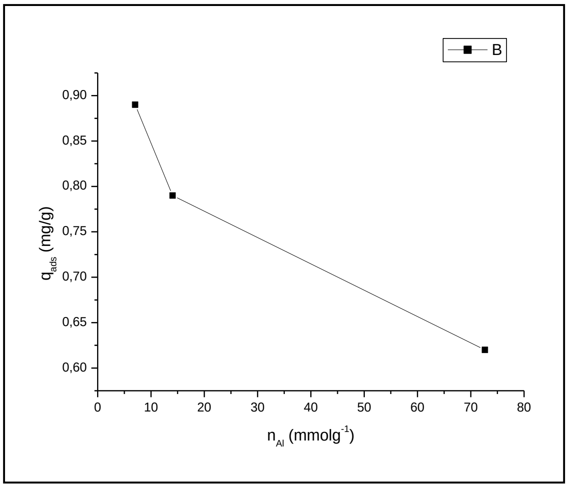


Figure 2.*Effect of Al content on the adsorption capacity. C_0 = 50 mg L^{-1}; agitation = 150 rpm pH=6; adsorbent dosage = 10 g L-1 and contact time 1 h.*

III.5. Effect of ionic strength

Obtained results (Figure 5) show that adsorption equilibrium is not affected by ionic strength of the solution. We observed a slight increase in the uptake of phenol with the increase in NaCl concentration, resulting from the reduction in the solubility of phenol caused by increase in the concentration of the electrolyte which is more soluble, leading to reduction in intensity of adsorbate-solvent interactions. Dong et al. [8], noted the same phenomenon in their study.

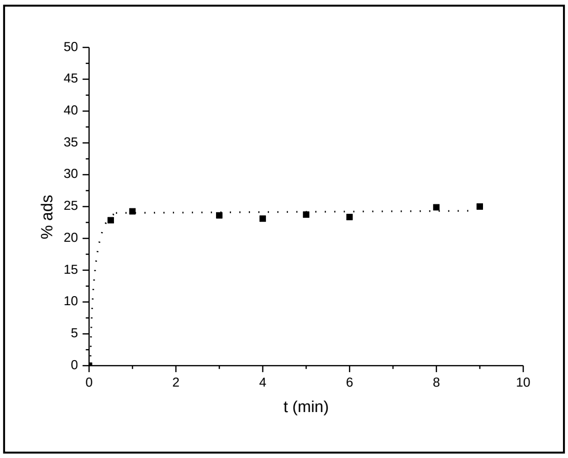


Figure 3.*Effect of contact time on phenol adsorption onto HFAU (60). C_0= 50 mg L^{-1}; agitation = 150 rpm; pH = 6; adsorbent dosage = 10 g L^{-1}.*

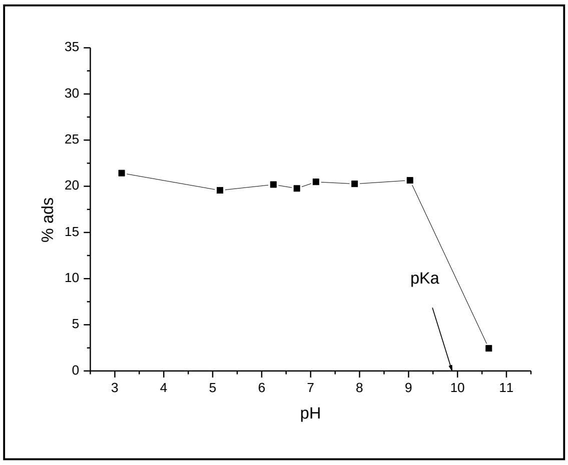


Figure 4. *Effect of the pH on the adsorption equilibrium of HFAU (60). Adsorbent dosage = 10 g L^{-1}; agitation = 150 prm, contact time = 1 h and C_0= 50 mg L^{-1}.*

III.6. Adsorption isotherms

Adsorption isotherms were carried out by varying the initial concentration of the adsorbate from 10 to 100 mg L^{-1}, which is the region of low concentration more appropriated to investigate adsorbent-phenol interactions. Obtained curves (*Figure 6*) show clearly a linear tendency with good correlation (R^2 = 0.99 for the three zeolites). The same type of isotherms was obtained by Roostaei et al. [16] and Khalid et al. [18]. This linearity illustrates a constant distribution between the two phases, characterized by a coefficient called distribution coefficient K_d ($K_d=q_{ads}/C_e$). This type of isotherm is indicative of an important competition between adsorbate and solvent for the occupation of the active surface. The other observation is the increase of isotherm slop with augmentation of Si/Al ratio, confirming the fact that aluminum of the zeolite affects the completion effect between water and phenol.

Table 3. *Parameter Values of adsorption models.*

	Langmuir			**Freundlich**				**D-R**		
Zeolite	q_{max} (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F	1/n	n	R^2	q_{max} (mg g^{-1})	E (kJ mol^{-1})	R^2
HFAU (5.2)	13.61	0.001	0.99	0.010	0.93	1.02	0.99	9.55	7.0	0.99
HFAU (30)	22.29	0.001	0.98	0.014	1.10	0.91	0.98	61.76	6.45	0.98
HFAU (60)	24.51	0.001	0.99	0.032	0.95	1.05	0.99	45.09	6.83	0.99

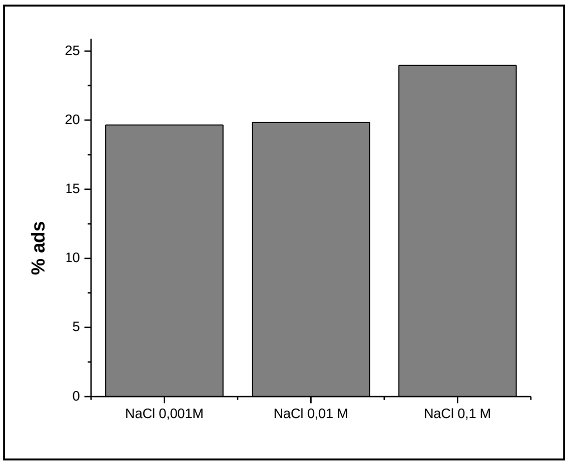


Figure 5. *Effect of the ionic strength on the adsorption equilibrium of the zeolite HFAU (60).* ***.*** *Adsorbent dosage = 10 g L^{-1};agitation = 150prm,pH = 6 contact time = 1 h and C_0= 50 mg L^{-1}.*

III.7. Modelisation of the adsorption equilibrium

The adsorption equilibrium was modeled by three two parameters models: Langmuir, Freundlich and Dubinin-Raduskevich (D-R.). Parameters of these models were calculated by the non-linear regression method. The calculations were effectuated by Origin 6.0 software with the function *non-linear curve* of the software. The results are illustrated on *Table 3*. As can be seen from *Figure 7*, experimental data are well fitted by the three models with a correlation of approximately 0.99 for each model. The values of E calculated by D-R model were less than 8 KJ mol^{-1}, indicating that adsorption of phenol is by physisorption. Values of parameter n of the model of Freundlich are close to 1 which resulting from linearity of isotherms. We also, noted that values of the Langmuir coefficient (K_L) and Freundlich (K_F) coefficient increase with the Si/Al ratio, indicating that adsorption become more favorable with increase in the hydrophobic character of the adsorbent. Applicability of the three models and linearity of the adsorption isotherms is due to the fact that the adsorption equilibrium is on the domain of the Henry low ($q_{ads} = KC_e$), since both concentration and adsorbed amount of phenol are very low.

This particular linear region observed in the beginning of each adsorption isotherm can be considered as simple and direct measure of the competition effect between the adsorbate and solvent for occupation of the surface (or sites) of the adsorbent

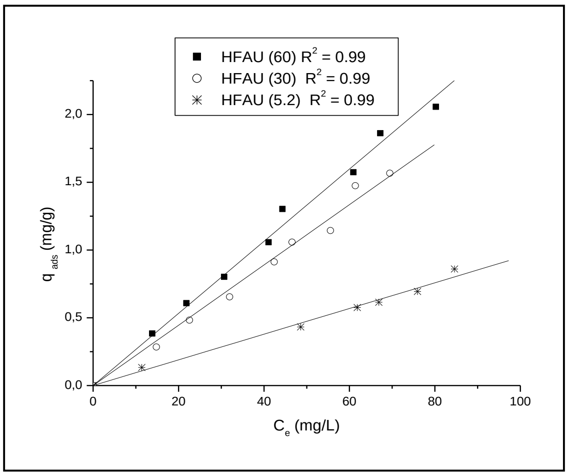


Figure 6. *Isotherms of adsorption. Agitation = 150 rpm, adsorbent dosage = 10 g L^{-1}, pH = 6, contact time = 1 h and T = 20±1°C.*

IV. Conclusion

The results obtained in this study show that zeolite Y has very interesting properties of adsorption and that the increase in the hydrophobic character which is related to Si/Al ratio increases capacity of adsorption of phenol in aqueous medium. We also found that adsorption was fast, supported at low values of pH and was not affected by ionic strength. Isotherms of adsorption obtainedare all linear and D-R model shows that adsorbent-adsorbate interactions are of physical nature ($E < 8$ kJ mol^{-1}). There for, for a significant increase of the adsorption of organic contaminants capacity onto FAU zeolite or other large pore zeolites, Si/Al ratio should be amplified to reach elevated values by post-synthesis treatment for example (dealumination by acid leaching) or even by design highly or purely siliceous zeolites.

V. References

1. Su-Hsia Lin, Journal of Environmental Management 90 (2009) 1336–1349.
2. C. Muniz-Lopez, J. Duconge, R. Roque-Malherbe, Journal of Colloid and Interface Science 329 (2009) 11– 16.
3. A. Kuleyin, Journal of Hazardous Materials 144 (2007) 307–315.
4. M. Sprynskyy, T. Ligora, M. Lebedynets, B. Buszewski, Journal of Hazardous Materials 169 (2009) 847–854.
5. S. R. Taffarel, J. Rubio, Minerals Engineering 23 (2010) 771–779.
6. B. Armagan , M. Turan, M. S. Çelik, Desalination 170 (2004) 33-39.
7. S. Yapar and M. Yilmaz, Adsorption 10 (2004) 287–298.
8. Y. Dong, D. Wu, X. Chen, Y. Lin, Journal of Colloid and Interface Science 348 (2010) 585–590.
9. W. Chunfeng, L. Jiansheng, W. Lianjun, S. Xiuyun, and H. Jiajia, Chinese Journal of Chemical Engineering 17(3) (2009) 513-521.
10. W. T. Tsai, K. J. Hsienb, H. C. Hsu, Journal of Hazardous Materials 166 (2009) 635–641.
11. C. K. Lee, S. S. Liu, L. C. Juang, C. C. Wang, K. S. Lin, M. D. Lyu, Journal of Hazardous Materials 147 (2007) 997–1005.
12. P. A. Mangrulkar, S. P. Kamble, J. Meshram, S. S. Rayalu, Journal of Hazardous Materials 160 (2008) 414–421.
13. M. Ghiaci, A. Abbaspur, R. Kia, F. Seyedeyn-Azad, Separation and Purification Technology 40 (2004) 217–229.
14. A. Metes, D. Kovacevic, D. Vujevic, S. Papic, Water Research 38 (2004) 3373–3381.
15. B. Okolo, C. Park, M. A. Keane, Journal of Colloid and Interface Science 226 (2000) 308–317.
16. N. Roostaei, F. H. Tezel, Journal of Environmental Management 70 (2004) 157–164.
17. B. Koubaissy, G. Joly, and P. Magnoux, Ind. Eng. Chem. Res. 47 (2008)9558–9565.
18. M. Khalid, G. Joly, A. Renaud, and P. Magnoux, Ind. Eng. Chem. Res. 43 (2004) 5275-5280.
19. I. Braschi, S. Blasioli, L. Gigli, C. E. Gessa, A. Alberti, A. Martucci, Journal of Hazardous Materials 178 (2010) 218–225.
20. A. Martucci, L. Pasti, N. Marchetti, A. Cavazzini, F. Dondi, A. Alberti, Microporous and Mesoporous Materials 148 (2012) 174–183.
21. G. Limousin, J.-P. Gaudet, L. Charlet, S. Szenknect, V. Barthès , Applied Geochemistry 22 (2007) 249–275.
22. D. D. Do, Adsorption analysis: equilibria and kinetics vol 2, Imperial College Press, 1998.
23. V. J. Inglezakis, Microporous and Mesoporous Materials 103 (2007) 72–81.
24. S. Vasiliu, I. Bunia, S. Racovita, V. Neagu, Carbohydrate Polymers 85 (2011) 376–387.

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