

REMOVAL OF HUMIC ACID USING ZEOLITE ZSM-5

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Abstract

The removal of humic acid from model and compost waters with adsorption onto zeolite was studied. Different types of zeolite were chosen for adsorption of humic acid from water. Following the preliminary tests, among the tested zeolites ZSM-5 Silicalite showed the best preliminary results, therefore, it was modified using TiO₂ in order to improve humic acid removal from water. Zeta potential was determined. The concentration of humic acid was measured spectrophotometrically. The efficiency of modified and non-modified zeolite for the adsorption of humic acid from model and compost waters was evaluated. The experiments were performed in a bed column.

Keywords: zeolite, humic acid, zeta potential, adsorption

1. INTRODUCTION

Zeolites can be found in natural or synthetic forms. Several methods can be used to synthesize the zeolite commercially in different sizes and structures, including various crystalline structures. Zeolites are used as adsorbent for organic and inorganic compounds due to their large surface area and negative surface charge. Mostly positive cations were studied using zeolites as adsorbent due to electrostatic attraction. On the other side humic acid could be unwanted in surface waters especially due to their yellow colour and substrate for microbiological growth (Sun and Lee, 2011). The adsorption of humic acid by surfactant modified zeolites has been investigated. (Li et al, 2011) The uptake of humic acid was substantially influenced by pH, increasing under acidic pH conditions. Zeolite 4A coated by ZnO has been successfully adapted for humic acid removal from drinking water sources (Wang et al, 2016). Modified zeolite exhibited enhanced adsorptive properties for humic acid in wide pH range. The results showed that electrostatic interaction plays a main role in the initial adsorption of humic acid. In the second step self aggregation is the most important. Zeolite synthesized from coal fly ash have been investigated in recent years for ions removal. It was modified by surfactant in order to remove humic acid (Li et al, 2011). The removal efficiency was comparable with the adsorption on granular carbon previously reported. Several studies have been published describing different methods of synthesizing monocrystalline ZSM-5 zeolites. (Nada and Larsen, 2017). Seed assisted method was developed for synthesis of zeolite ZSM-5 without organic template. Different influences were studied, especially dependence of crystal quality on time and temperature. The adsorption mechanism of humic acid on TiO₂ surface was studied (Sun and Lee, 2012). The experimental data was fitted using the Langmuir–Freundlich adsorption model. A newly formed Ti-bounded compound detected after the adsorption process proved the validity of surface complexation mechanism. The carboxylic group would most likely bound through the oxygen atom to the Ti⁴⁺ cations.

Zeolite ZSM-5 Silicalite is a promising support for TiO₂ because they have regular pores and channels in the order of 0.44–1.4 nm that can confine substrate molecules, thereby enhancing adsorption and photo-catalysis. TiO₂ supported on zeolite combines the adsorptive capability of TiO₂ with that of zeolite, thus resulting in a synergistic and enhanced adsorbability efficiency (Alshameri et al, 2014). Surface properties are important to identify the interaction between HA and TiO₂ at different pH condition. Zeolite ZSM-5 Silicalite was used in this study for HA adsorption. Since preliminary test showed that powdered zeolites could not be easily separated from humic acid solution, Zeolite ZSM-5 Silicalite was granulated.

2. MATERIALS AND METHODS

2.1. Materials

Zeolite ZSM-5 Silicalite is synthetic zeolite, produced in Slovene company Silkem. Chemical formula is $\text{Na}_n\text{Al}_n\text{Si}_{96-n}\text{O}_{192}\cdot 16\text{H}_2\text{O}$ ($0 < n < 27$) [13]. Pentasil units in zeolite are linked to form pentasil chains, and mirror images of these chains. Both are connected via oxygen bridges to form corrugated sheets with 10 ring-holes. Each sheet is linked by oxygen bridges to the next to form the 3-D structure. Specific adsorption properties are connected with such structure. The pores are 5,3Å middle size. Zeolites are thermally resistant.

Modification of zeolite was done by using TiO_2 (Merck, Millipore). TiO_2 is not toxic. The size of anatase crystals was <25 nm, the share of anatase was 70 %, rutil 15 %, and the rest was amorphous TiO_2 .

Humic acid stock solution was prepared by dissolving 5 g of Sigma Aldrich humic acid in 1L 0,1 M NaOH. The stock solution was filtered through a filter paper with 0,45µm pore size (Whatman) to remove all the suspended solids and stored at 4 °C.

Surface water samples were taken from river Drava, Maribor, Slovenia for preliminary tests in order to determine which of the chosen zeolite would show the highest adsorption capacity.

Compost leachate samples were taken from lagoon in Compost company Kogal, Šentilj, Slovenia.

2.2. Methods

The crystallization seed for the zeolite ZMS-5 Silicalite granules were prepared according to the literature (Fakin et al, 2015). Granulation of zeolite ZMS-5 Silicate (Z) was done with 1400 g of zeolite ZSM-5 Silicalite and 600 g of attapulgit as binding media. The mixture was mixed in Eirich mixer by adding water. Granules were formed with diameter 1 mm. Zeolite was dried at 105 °C and activated in the laboratory calcining kiln for three hours at 350 °C. TiO_2 share in modified zeolite granules (ZTi) was 1,55 %. Granulation was done with 1400 g zeolite ZSM-5 Silicalite and 600 g of attapulgit as binding media and 30 g of TiO_2 . The mixture was mixed in Eirich mixer by adding water. Granules were formed with diameter 1 mm. Drying of the granules was conducted in a laboratory oven at 105 °C and further activation of the samples in the laboratory calcining kiln for three hours at 350 °C. Prepared zeolites are seen from Fig. 1.



Fig. 1. Zeolite granules (left) and zeolite granules modified by TiO_2 (right)

Bed column experiments with zeolite were performed. Two sets of experiments were performed once with zeolite and once with TiO_2 modified zeolite at the same conditions. The bed height was 50 cm, diameter of the column 1 cm. The standard solution of humic acid was poured through the column at different flows. The experiments were repeated with compost leachate at the optimum flow. The column is seen from Fig. 2.



Fig. 2. Adsorption column with zeolite granules

Removal efficiencies R (%) were determined according to equation 1:

$$R \text{ (%) } = (A_0 - A) / A_0 \cdot 100 \text{ (%)}$$
(1)

where

A_0 = measured initial absorbance at 254 nm

A = measured absorbance at 254 nm after the adsorption

3. RESULTS

3.1. Characterisation of zeolites

It is known from the literature that zeolites have during the pH range 2-9 negative zeta potential (Sun, 2012). Fig. 3 displays the zeta potential of granulated ZMS-5- TiO_2 at 10 ppm. The surface was positively charged in acidic region and negatively in alkaline region. The negative and positive charge are connected to the TiO_2 species. The point of zero charge (PZC) was obtained at 6,6. The value is well in accordance with other research (Sun, 2012) where PZC at 6,5 was determined. The same author reported that humic acid molecules are negatively charged from pH 2 to pH 9, however the surface charge is more negative towards alkaline region. Zeolite surface charge is negative as well. Carboxylic groups undergo dissociation in acid region and play an important role during adsorption in acidic region.

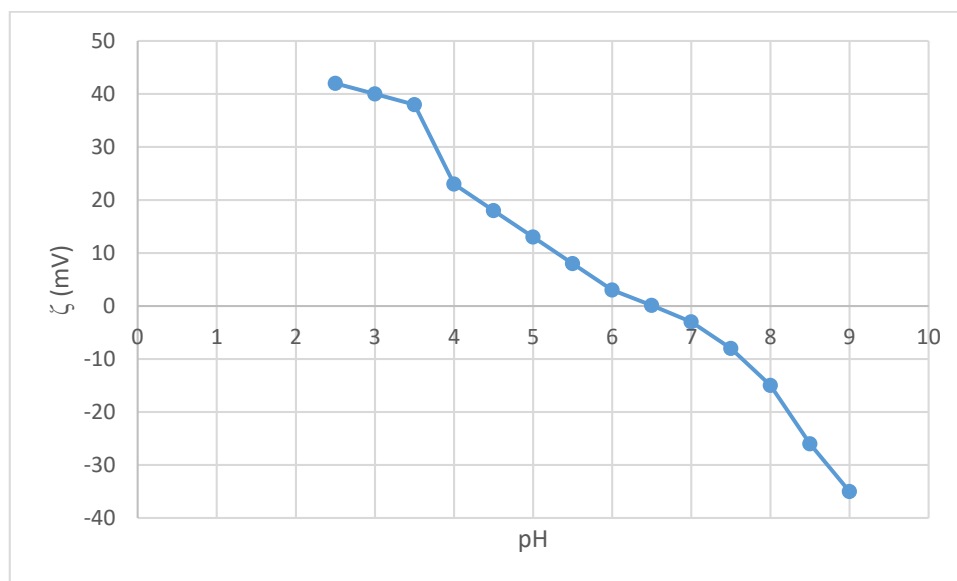


Fig. 3. Zeta potential of granulated ZMS-5-TiO₂

The working solution was prepared from stock solution by diluting to concentration to concentrations from 1 mg/L to 10 mg/L. Calibration curve for humic acid was done (Fig. 4). Above 10 mg/L the calibration curve was not linear.

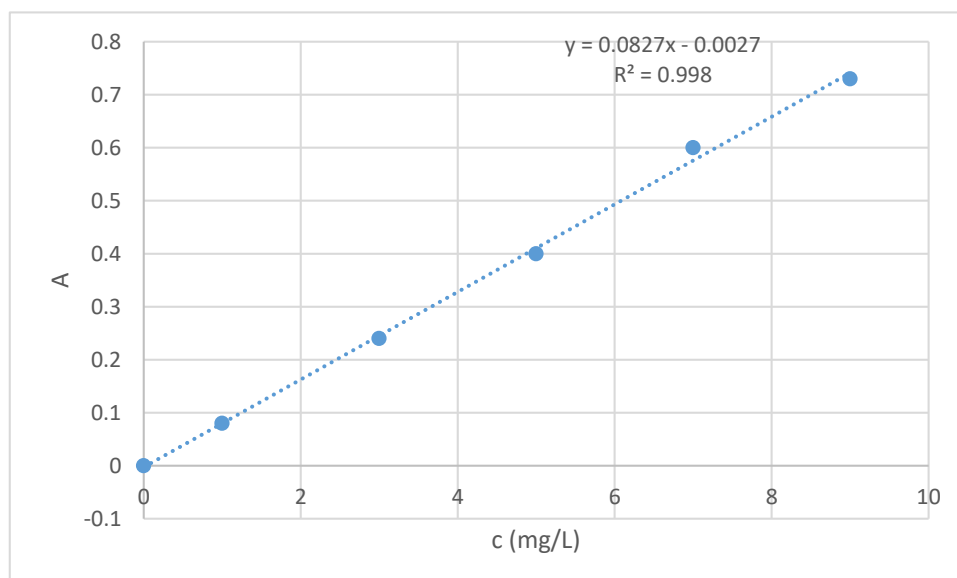


Fig. 4. Calibration curve

3.2. Preliminary results

Among several types of synthetic zeolites (all purchased from Silkem, Slovenia) the one was chosen for modification which removed the most humic acid from surface water. Absorbance measured at 254 nm showed the maximum reduction by using ZMS-5 Silicalite. The measured parameters improved only by using ZMS-5 Silicalite, while with others the values of absorbance and turbidity remain unchanged. Turbidity (Turb) in sample with ZP4A increased because the granules of ZP4A were not prepared according to the recipe and they have broken up.

Table 1. Measured parameters in preliminary tests

	A254	pH	Turb (NTU)
Untreated Water sample	0,0924	7,7	2,14
ZMS-5 Silicalite	0,0411	8,4	1,35
ZMS (MFI)	0,0923	9,4	2,14
ZP13X	0,0801	8,9	2,14
ZP4A	0,0920	10,1	5,0

The working solution was prepared from stock solution by diluting to concentration 60 mg/L. 50 ml of such solution was poured into the column with zeolite (Z). The contact time was set to 10 min and was prolonged to 1h. The pH was measured at 8. The sample was gathered into the Erlenmeyer flask. The concentration of humic acid was measured in effluent solution. The same amount of the humic acid solution with the same concentration was tested using modified zeolite (ZTi). Results are presented in Fig.5. The removal efficiency of humic acid (R) was better using modified zeolite. The optimum value was 63 % using TiO₂ modified zeolite. As seen from Fig. 5, in the acid region the adsorption was comparable. The removal efficiency was around 22 % using TiO₂ modified zeolite. In alkaline region the results were worse. The removal efficiency was below 10 %.

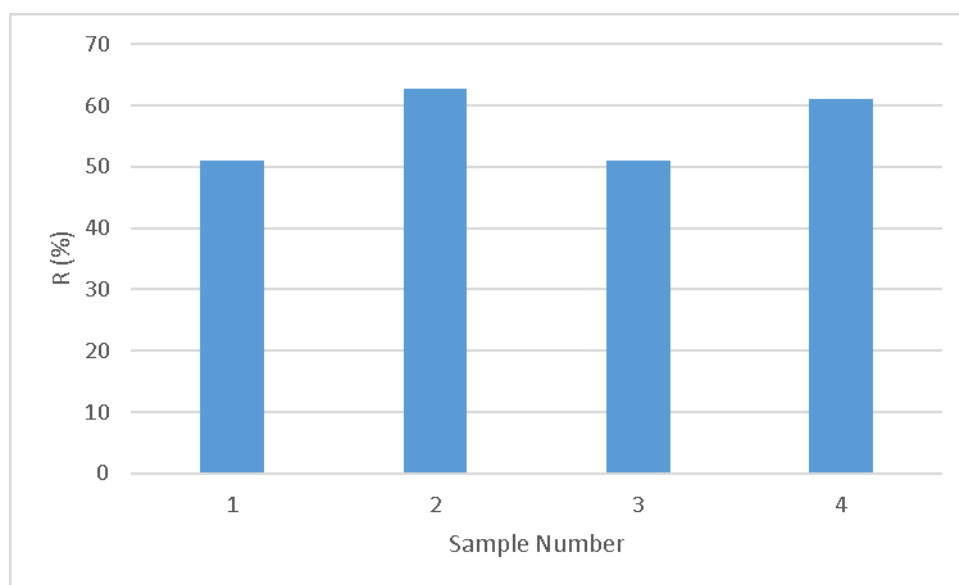


Fig. 5. Removal of humic acid: 1 acid Z, 2 acid ZTi, 3 neutral Z, 4 neutral ZTi

4. DISCUSSION

The zeta potential curve evidenced that the main factor that affected the adsorption extent was of electrostatic origin as agreed by many researchers. At pH < 7, negatively charged HA would adsorb on positively charged ZTi granule due to the electrostatic attraction. At pH > 7, both negatively charged HA and ZTi granule generated a strong electrostatic barrier which would inhibit the adsorption process. However, HA adsorption did occur above PZC suggesting that adsorption other than the electrostatic interaction between HA and TiO₂ microsphere surface must exist. Hence it was suggested that the neutral surface species of TiO₂ (–TiOH) would interact with the deprotonated functional groups of HA (L⁻) via ligand exchange to form surface complexes as agreed by Sun and Lee (2012). A negative potential profile was developed around TiO₂ at all pH values after attaining adsorption equilibrium. The

charge reversal of TiO_2 microsphere from positive to negative at lower pH values indicated that bound organic polyanions had smeared out the differences between the surface properties of oxides because of covering the most reactive conditionally charged Ti-OH sites. The adsorption of HA would neutralize the positive charges of ZTi. The surface charge compensation might lead to electrostatic repulsion between the free HA molecules and the HA/ TiO_2 complex that would strongly inhibit further adsorption of the negatively charged HA.

4.1. Compost leachate adsorption results

Compost leachate was sampled. In time units from 10 min to 2 hours the removal efficiency was measured. Results are presented in Fig. 6. It is seen that the removal efficiency increased with time. It was always a little better using modified zeolite, but lower than in surface water samples. It was expected due to the fact that other organic particles interact with zeolite surface and, in this way, other molecules compete with the humic acid. If so, zeolite adsorption ability for humic acid in compost leachate is limited, because surface of zeolite is surrounded by other organic and inorganic compounds in compost leachate. Although the leachate was filtered before adsorption, still many colloids and dissolved ions remained in filtered compost leachate effluent as reported from our previous study (Simonic, 2017).

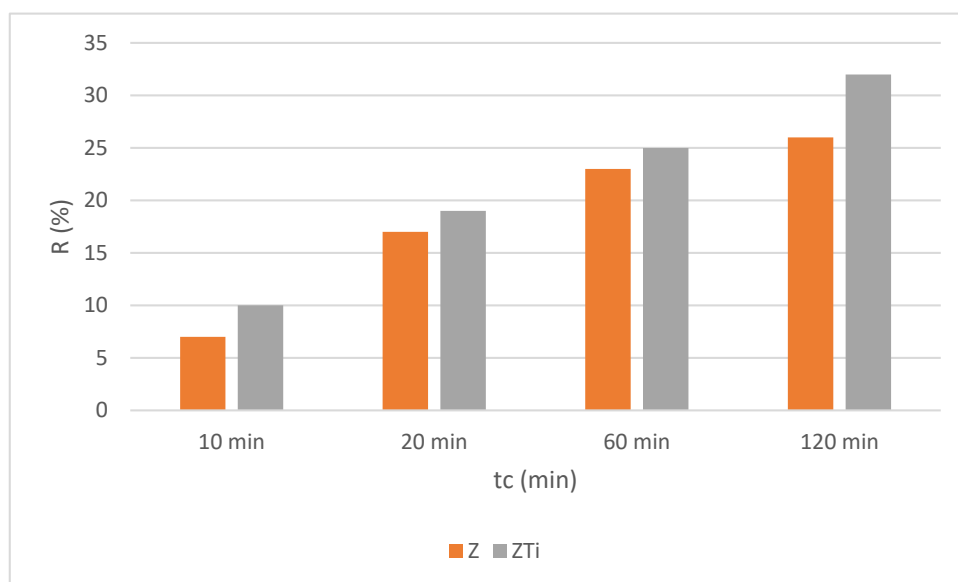


Fig. 6. Removal efficiency depended of time

5. CONCLUSIONS

The removal of humic acid from model and compost waters with adsorption onto zeolite was studied. Zeolite ZSM-5 Silicalite has shown to be the most promising among tested zeolites, therefore, it was granulated and modified with TiO_2 . The efficiency of modified and non-modified zeolite for the adsorption of humic acid from model and compost waters was studied. The experiments were performed in a bed column. The effect of the contact time and the pH of the model water solutions were studied. Based on the measured absorbance values at 254 nm for experiments carried on at the contact time 20 mins we came to the conclusion that the highest efficiency was achieved in acidic and neutral model water solution. After the treatment with modified zeolite the efficiency was 62,4 % and after non-modified zeolite 50,9 %. Under the basic pH conditions the efficiency was worse. Experiments were carried on at the lowest contact time with compost. The efficiency of adsorption with the use of modified versus non-modified zeolites in the compost water at the contact time 2 h was 9,9 % higher.

ACKNOWLEDGMENTS

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REFERENCES

1. Liu, S, Lim,M, Amal R 2014, "TiO₂-coated natural zeolite: Rapid humic acid adsorption and effective photocatalytic regeneration", *Chemical Engineering Science*, vol. 105, pp 46–52.
2. Li, C, Dong, Y, Wu, D, Peg, L, Kong, H 2011, "Surfactant modified zeolite as adsorbent for removal of humic acid from water", *Applied Clay Science*, vol. 52, no. 4, pp. 353-357.
3. Rodrigues, A, Brito, A, Janknecht, P, Proenca, MF, Nogueira RN 2009, "Quantification of humic acids in surface water: effects of divalent cations, pH and filtration", *Journal of Environmental Monitoring*, vol.11, pp. 377-382.
4. Fakin, T, Ristić, A, Mavrodinova, V, Zabukovec Logar, N 2015, "Highly crystalline binder-free ZSM-5 granules preparation", *Microporous and mesoporous materials: zeolites, clays, carbons and related materials*, vol. 213, pp. 108-117.
5. Alshameri A, Yan C, Lei X 2014, "Enhancement of phosphate removal from water by TiO₂/Yemeni natural zeolite: Preparation, characterization and thermodynamic", *Microporous and mesoporous materials: zeolites, clays, carbons and related materials*, vol. 196, pp. 145-157.
6. Simonic M 2017, "Compost leachate treatment using polyaluminium chloride and nanofiltration", *Open Chemistry*, vol. 15, pp. 1-6.
7. Sun, DD, Lee PF 2012, "TiO₂ microsphere for the removal of humic acid from water: Complex surface adsorption mechanism", *Separation and Purification Technology*, vol. 91, pp. 30-37.