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FORMALDEHYDE REMOVAL FROM WASTEWATER APPLYING NATURAL ZEOLITE

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Abstract. Formaldehyde is one of the most chemically active compounds which is discharged with untreated or just partially treated industrial wastewater. It is hazardous for environment and humans. Formaldehyde vapors can strongly irritate skin, can cause damage to eyes and harm respiratory tract. As long as formaldehyde causes a toxic effect on environment and living organisms, it is necessary to remove it from wastewater which is directed to natural water. There are many methods used for formaldehyde removal from wastewater: biological method, evaporation, membrane separation method. Most of them have disadvantages. Adsorption method has many advantages: it is fast, cheap, and universal, and can be widely used, therefore it was chosen for this research.
Experiment was carried out with natural zeolite in different contact time with different concentration formaldehyde solutions. Concentration of formaldehyde was determined applying the Photocolorimetric Method. Method is based on reaction of formaldehyde with chromotropic acid and determination of formaldehyde concentration. Determined average sorption efficiency was highest when formaldehyde concentration was lowest, e. g. 2 mg/l (45.94%) after eight hours of contact time with adsorbent. Sorption efficiency was increasing when the contact time increased, but when the contact time increased to 12 hours, sorption efficiency stayed the same because of the saturation of zeolite.

Keywords: formaldehyde, water, pollution, wastewater, removal, zeolite, adsorption.

Introduction

Water resources are the most important for natural ecosystems and also for human development but they are becoming limited because of the growing population, increasing urbanization, and climate changes. The main reason is water pollution, which is caused by the discharge of untreated or just partially treated industrial pollutants into the natural ecosystems, it causes serious problems in them (Salman *et al.* 2011) These industrial pollutants contain a lot of different organic and inorganic pollutants. For example: phenols, formaldehyde, dyes, and heavy metals. They are the main water pollutants (Athar *et al.* 2011).

Formaldehyde is one of the most chemically active compounds found in industrial wastewater. It has many industrial and non-industrial applications (Bel'chins'ka 2013). It is used in production of resins, adhesives and hardboards, fungicides, pharmaceutics, paper, etc (Ceolity 2003). This compound is applied to sterile sanitary and medical parts (Koziol *et al*. 2013).

In water, formaldehyde is hydrated and usually is found in the form of methylene glycol and its oligomers (Bullut, Tez 2006). It is classified as a carcinogenic substance and causes skin damage, inflammatory lesions, and allergic reactions. Formaldehyde vapours can strongly irritate skin, can cause damage to eyes and harm respiratory tract (Athar *et al.* 2011). As long as formaldehyde causes a toxic effect on environment and living organisms, it is necessary to remove it from wastewater which is directed to natural waters (Koziol *et al.* 2013).

Formaldehyde is water soluble so it can easily get in wastewater from different types of industry (Crini, Badot 2010). It can be hazardous for the environment and humans (Briški *et al.* 2012). In many industries the wastewater contaminated with formaldehyde is collected into lagoons to evaporate over time. This causes formaldehyde ingression into the atmosphere and further pollution of the air (Bagheri *et al.* 2014). Adsorption method has many advantages: it is fast, cheap and universal (Boonamnuayvitaya *et al.* 2005).

Sorbents are insoluble substances or mixture of them, which attaches and keeps pollutants in their molecular structure (absorbents) or in their porous and capillary surface (adsorbents) (Delle Site 2001).

Zeolite is one of the most popular adsorbents. Structure of zeolite is similar to the frame and it forms great internal and external surfaces on which ion exchanges and chemical reactions may take place. Zeolite pores cover 50% of zeolite volume (Buszewki *et al.* 2006). A porous zeolite structure helps to collect and maintain the collected particulate matter, which can be up to 4 microns or larger (Natūralus ceolitas 2012).

Zeolite (clinoptilolite) generally have a negative charge, so it has the ability to exchange ions (Elshorbagy, Chowdhury 2013). These result in a zeolite to absorb ammonia ions (NH_4^+) and cations, which dissolve in water. Zeolite clean water by separating heavy metals such as Pb, Cu, Cd, Zn, Co, Cr, Mn and Fe (Natūralus ceolitas 2012).

Clinoptilolite may detain solid, liquid and gaseous substances on its large internal absorbing surface. The channel dimensions are large enough to allow the molecule, which is a few tenths of a size according to the nanometric scale, penetrate, while these channels are too small to contain large complex molecules such as amino acids, vitamins and other biological macromolecules. Clinoptilolite cell acts as a selective adsorbent sieve, during which only some molecules may pass.

The ability of zeolites to sorb selectively is widely used in different groups of science and engineering. Zeolites are selective for different types of gasses and liquids and this property can be widely applied. Cation-exchange method allows influencing the sorption properties of zeolites. While applying for the inorganic ionites, the ion exchange is the ability or property of solid phase to exchange ions with liquid or gaseous electrolytes without destruction of the original crystal structure of zeolite (Ceolity 2003).

The aim of the work is to investigate the opportunities of using natural zeolite for removing formaldehyde from wastewater.

Methodology and relevance of the research. To evaluate zeolite as a potential adsorbent to remove formaldehyde from industrial wastewater the determination of physical (bulk density) and chemical (pH) properties were applied in this research.

1) *Determination of dry bulk density:* determination of dry bulk density is based on dry matter weight and the occupied volume ratio (Dadey *et al.* 1992) using a standard measuring container (ISO 567).

The standard container was weighted and placed on a horizontal surface. Then adsorbent samples were poured into the container until the container begins to crumble over the edges. The heap is scraped off. Loaded container was weighed and bulk density was calculated. This experiment was repeated with three different formaldehyde fractions (1–2; 2–4; 4–6 mm) to evaluate which size of zeolite particles has the lowest dry bulk density (dry bulk density is inversely related with porosity of sorbent, the lower dry bulk density value – the more porous sorbent is).

2) *Static formaldehyde sorption from solution applying adsorbent* – the following parameters are assessed while performing these experiments (Formaldehyde 2002):

1. The pH of the solution;
2. The formaldehyde concentration in the solution;
3. The adsorption time.

3) *Assessment of the influence of pH on formaldehyde sorption* – the influence of the pH of the formaldehyde solution on the adsorption results was evaluated by changing the pH of the solutions. The reason of the pH change is the covering of the recommended pH values of the cleaned sewage stated in the regulation of sewage management, ranging from 6.5 to 8.5. For that reason and for adsorption process deeper analysis pH interval was increased, the solutions were prepared with the following pH: 3; 5; 7. In order to ensure the quality of the results, pH of the solutions are measured before and after sorption. PH of the solutions is measured with Mettler Toledo Seven Multi pH meter.

4) *Effect of initial concentration on formaldehyde removal:* the solutions were modelled with constant adsorbent dosage (1 g), pH, i.e. 0.1 M NaOH and 0.1 M HNO_3 was used to adjust pH. Different initial concentrations of formaldehyde were selected for researches: 1 MCL = 2 mg/l, 2 MCL = 4 mg/l, 3 MCL = 6 mg/l, 5 MCL = 10 mg/l and 10 MCL = 20 mg/l.

Adequate formaldehyde was chosen as a source of formaldehyde (Delle Site 2001). Formaldehyde was mixed with 800 ml of deionized water and diluted till the sign in a 1000 ml capacity flask. 1 g of adsorbent was mixed with 100 ml of formaldehyde solution containing different concentrations of formaldehyde, using capped bottles (100 ml) (Cussler *et al*. 2002). The suspensions were filtered thorough glass filters 0.45 μm and the concentration of formaldehyde in the filtrates as well as in the initial solutions was determined using spectrophotometer. Concentration of formaldehyde was determined applying photocolorimetric method. Method based on reaction of formaldehyde with chromotropic acid and determination of formaldehyde concentration. The concentration of formaldehyde was determined in the aqueous solution from formaldehyde calibration curve by measuring optical density at $\lambda = 584$ nm with photocolorimeter in 1 cm length cells. Concentration of formaldehyde was determined based on measuring of optical density of formaldehyde and chromotropic acid product (purple color). Also formaldehyde was determined in the blank solution (chromotropic acid plus sulphuric acid) to adjust for possible contamination of chemical reagents (Dąbrowski 2001).

The experiments of static formaldehyde adsorption from aqueous solution are performed by mixing an adsorbent sample with the formaldehyde concentration solution on a 1:100 ratio of adsorbent and solution mass, i.e. 1 g of adsorbent and 100 ml of aqueous solution (Gang *et al.* 2001).

5) *Effect of sorption time on removal of formaldehyde:* The sorption time is assessed by analyzing the static formaldehyde sorption from the aqueous solution. The aim of these experiments is to determine the duration of sorption time and when the balance of adsorption is achieved. With this purpose, the following durations of 5 min, 10 min, 30 min, 60 min, 180 min, 300 min, 480 min, 720 min.

The samples were then placed on A. C. Gerhardt GmbH & Co.KG – Rotoshake RS12 – Elution Shaker and shaken at the room temperature of 20–22 ºC. Batch studies were used to determine the equilibrium time for the adsorption of formaldehyde by adsorbent. Adsorption equilibrium is achieved when the analysed concentration of the formaldehyde in the solution remains unchangeable. All samples with 1 g of adsorbent were added to the formaldehyde solution at the different pH and it was shaken for a period of time. The samples were then filtered (using glass filter with 0.45 µm pores) and the filtrate formaldehyde ion concentrations were measured. These experiments were conducted three times and average values were calculated.

6) *Statistical analysis*

Each analysis was prepared and analyzed in triplicates. For quality assurance the measurements were carried out three times and calculated the average of the results of measurement errors. The statistical analysis was performed using Excel 2013 program. The results of arithmetic mean values with standard deviation values were presented in graphical expression of the results.

Correlation technique was used to investigate the relationship between two variables. Pearson's correlation coefficient shows the relationship strength between two variables.

Results of sorption efficiency researches

Evaluation of dry bulk density:

Results of dry bulk density of different zeolite fractions are displayed below in Table 1:

1–2 mm fraction of adsorbent was chosen for experimental research. Also Croatian scientists (Kučic *et al.* 2012) evaluated sorption of ammonium effectiveness dependence on sorbent fraction (1–2 mm fraction was evaluated as the most effective).

Table 1. Dry bulk density according sorbent fraction

Sorbent fraction, mm	Dry bulk density, g/cm³
1–2	0.87± 0.05
2–4	0.88± 0.05
4–6	0.88± 0.05

Sorption efficiency evaluation: Concentration of formaldehyde after sorption process in every sample was calculated using formaldehyde calibration curve. Results are displayed below in Figures 1–5:

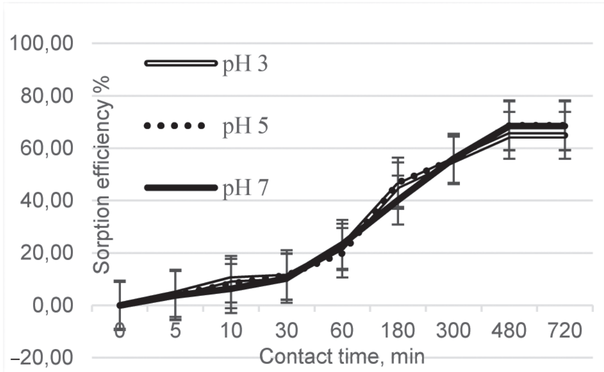

Fig. 1. Sorption efficiency in 2 mg/ formaldehyde solution (dependence on time and pH value with standard deviations)

As we can see in Figure 1, sorption efficiency was increasing by increasing contact time with adsorbent. Adsorption equilibrium is achieved after some time (in this case – after 8 hours). The highest efficiency of sorption was reached after eight hours of contact time (formaldehyde concentration in solution was 2 mg/l). After that, adsorption efficiency stayed stable, because of saturation of zeolite. Based on calculated Pearson`s correlation coefficients (between contact time and adsorption efficiency) we can make a conclusion that adsorption efficiency when using different pH values have strong relation with contact time with sorbent (r = from 1.0 to 0.5 in 95% confidence level).

Figure 2 graphically shows relationship between contact time and sorption efficiency in different pH values. The

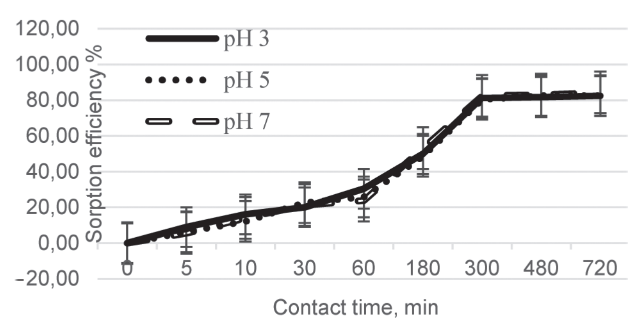

Fig. 2. Sorption efficiency in 4 mg/l formaldehyde solution (dependence on contact time and pH value with standard deviations)

highest efficiency was after 8 hours, when pH = 5 (68.79%). Sorption efficiency was increasing by increasing contact time with adsorbent. The adsorption equilibrium was reached after 8 hours in pH 5 solution (53.52%). After when contact time was longer than 8 hours, adsorption efficiency was no increasing anymore. It stayed stable. Pearson`s correlation coefficients showed strong relationship between contact time and adsorption efficiency (values of *r* were between 0.5 to 1 in 95% confidence level).

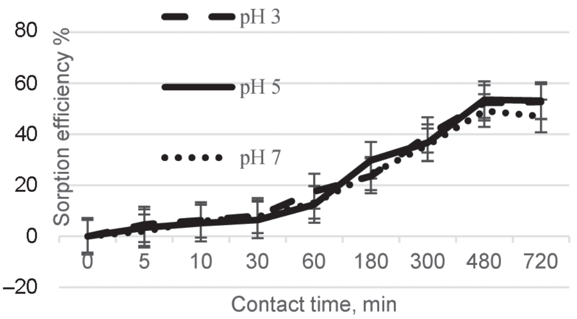

Fig. 3. Sorption efficiency in 6 mg/l formaldehyde solution (dependence on time and pH value with standard deviations)

The highest sorption efficiency in 6 mg/l formaldehyde solution was reached after 8 contact hours with zeolite same as in other solutions. Except there is one difference – sorption efficiency started to decrease with increasing formaldehyde concentration in solution. In Figure 1 the highest efficiency was 82.44%, and in Figure 3 only 53.62%, so it is possible to argue that saturation of zeolite affects adsorption efficiency. There is no significant relationship between pH value and sorption efficiency.

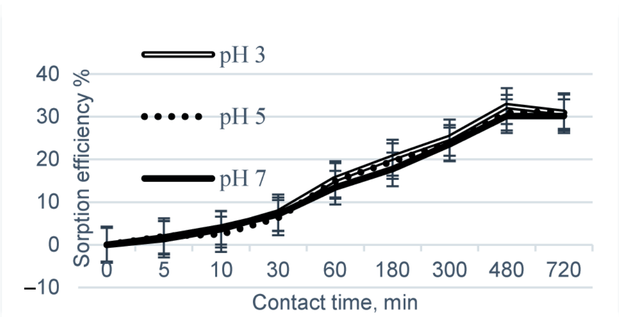

Fig. 4. Sorption efficiency in 10 mg/l formaldehyde solution (dependence on contact time and pH value with standard deviations)

The highest efficiency was after 8 contact hours – 32.51% (pH = 3). All Pearson`s correlation coefficients show strong relationship between contact time and sorption efficiency (values of r are equal to ~0.9 in 95% confidence level). Sorption efficiency is lower than in lower concentration formaldehyde solutions, so there is a tendency of saturation of natural zeolite affecting sorption efficiency.

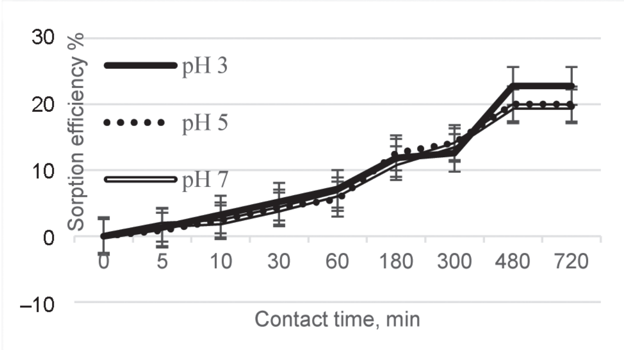

Fig. 5. Sorption efficiency in 20 mg/l formaldehyde solution (dependence on contact time and pH value with standard deviations)

The highest efficiency was after 8 contact hours – 22.76% (pH = 3). To compare it with lowest formaldehyde concentration solution (2 mg/l), sorption efficiency decreased almost 60%. So we can make a conclusion that higher formaldehyde concentration negatively affects sorption efficiency.

Average sorption efficiency was highest when formaldehyde concentration was 2 mg/l. It started to decrease with increasing initial formaldehyde concentration. It means that the adsorption is highly dependent on initial concentration of formaldehyde. It is because of that at lower concentration, the ratio of the initial number of formaldehyde molecules to the available surface area is low subsequently the fractional adsorption becomes independent of initial concentration (Arivoli *et al*. 2010).

Sorption efficiency arithmetical mean was calculated after different contact time with zeolite samples, to evaluate which contact time is most effective on sorption efficiency. After 8 hours adsorption reached equilibrium average efficiency was 58.54%. To compare it with shortest contact time (5 min) it is 55% higher.

After 12 hours (720 minutes) sorption efficiency was not increasing anymore because of saturation of sorbent.

The correlation between pH values and sorption efficiency was not significant, Pearson`s correlation coefficients were between 0.1 to 0.3 or from –0.1 to 0.1, so it means that relationship is weak or there is no relationship at all. In this case, there were no significant relationship (95% confidence level).

Conclusions

1. Results showed that dry bulk density was lowest when using 1–2 mm fraction of zeolite (0.87± 0.05). Dry bulk

density is inversely related to the porosity of natural zeolite. The lower dry bulk density means higher porosity. This property increases sorption efficiency.

2. Determined average sorption efficiency was highest when formaldehyde concentration was lowest, e.g. 2 mg/l (45.94%). The lowest sorption efficiency was in 20 mg/l solution of formaldehyde, main reason: saturation of zeolite.
3. Sorption efficiency increased with increasing of a contact time with zeolite, the lowest average sorption efficiency was after 5 minutes (3.42%) and the highest after 8 hours (58.54%), adsorption process reached equilibrium. After 12 contact hours average sorption efficiency was not higher than after 8 hours, because of saturation of zeolite.
4. Results showed that there was no significant correlation between pH of solution and sorption efficiency (Pearson`s correlation coefficients are from 0.1 to 0.3, or even from –0.1 to 0.1 so it means that there is no relationship between pH value and formaldehyde sorption efficiency in 95% confidence level).
5. The highest sorption efficiency was established after 8 hours of contact time with zeolite, using 2 mg/l formaldehyde solution (85.70%).
6. Results showed that adsorption capacity of zeolite was increasing when contact time was increased. Initial concentration of formaldehyde also affected adsorption capacity of zeolite. It was determined that the highest adsorption capacity was after 8 hours of contact time when formaldehyde concentration was 2 mg/l.

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FORMALDEHIDO ŠALINIMAS IŠ NUOTEKŲ PANAUDOJANT GAMTINĮ CEOLITĄ

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Santrauka

Formaldehidas yra vienas iš aktyviausių junginių, kuris išleidžiamas į aplinką kartu su nevalytomis ar iš dalies išvalytomis gamybinėmis nuotekomis. Jis yra pavojingas tiek aplinkai, tiek žmonėms.
Formaldehido garai stipriai dirgina akis ir kvėpavimo sistemą. Kadangi formaldehidas yra pavojingas žmonėms ir visiems gyviems organizmams, jis turi būti šalinamas iš gamybinių nuotekų.
Sorbcijos metodas turi daug privalumų: jis yra greitas, pigus ir universalus, todėl vienas iš labiausiai perspektyvių vandens valymo metodų – sorbcija. Tai pagrindinė priežastis, kodėl sorbcinis metodas buvo pasirinktas eksperimentiniams tyrimams.
Eksperimentiniai tyrimai buvo atlikti naudojat gamtinį ceolitą, buvo parinktas skirtingas formaldehido tirpalo kontakto laikas su adsorbentu ir matuojama teršalų koncentracija po kontakto su adsorbentu. Šis metodas yra paremtas formaldehido reakcija su chromotropine rūgštimi. Sorbcijos efektyvumas augo ilgėjant kontakto su ceolitu laikui, tačiau po 12 valandų efektyvumas nebedidėjo dėl to, kad sorbentas įsisotino.

Reikšminiai žodžiai: formaldehidas, vanduo, tarša, nuotekos, pašalinimas, ceolitas, adsorbcija.