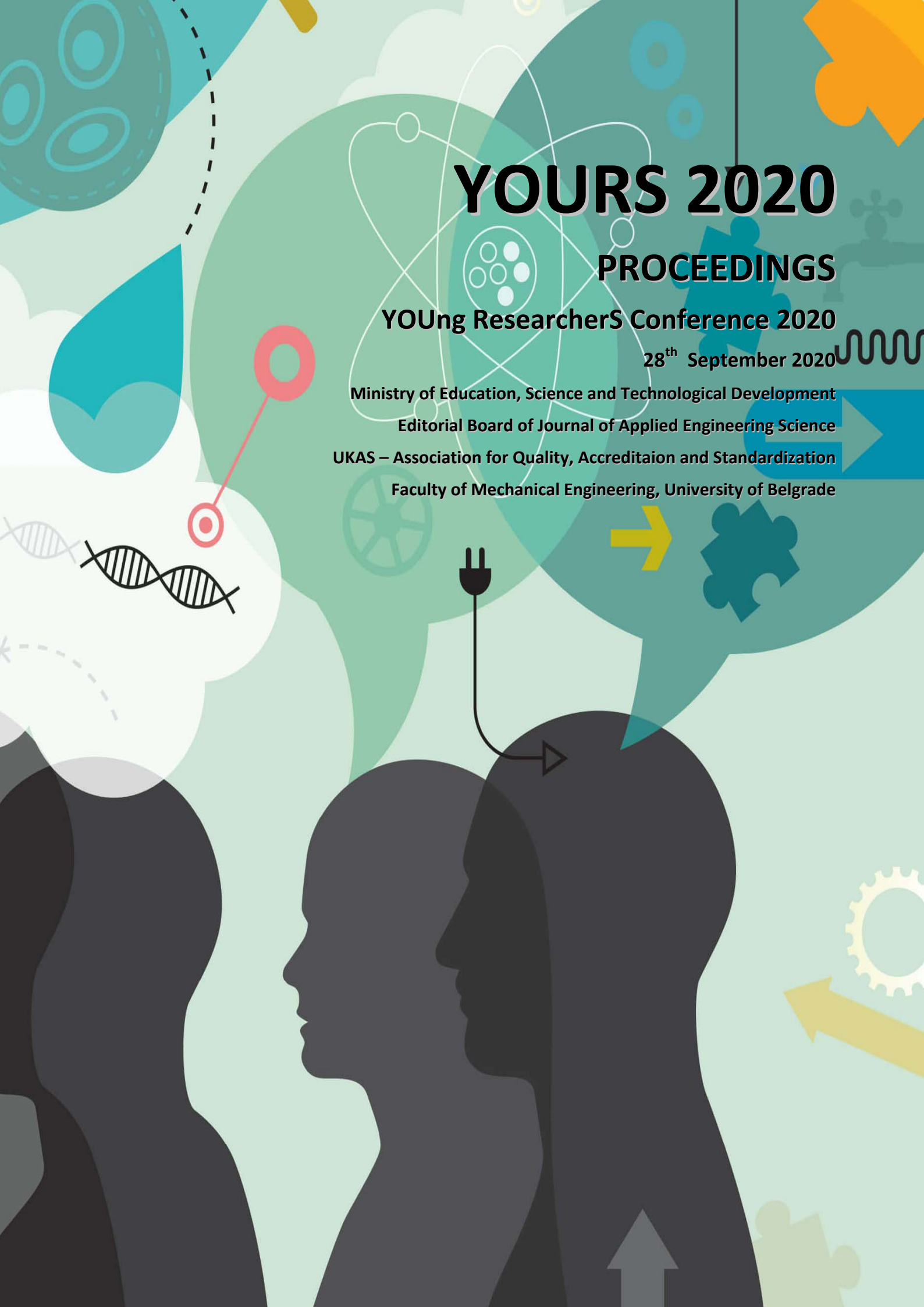

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ADJUSTING PH PZC VALUE DURING AND AFTER ADSORBENT PREPARATION

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Summary: Point of zero charge (PZC) is one the most valuable parameter of adsorbent preparation process, in wastewater management. Although, this parameter may be determined measuring the electrokinetic potential (zetta potential) as the function of pH; material engineers oftenrely on pH PZC value which may be easily determined and can give usefuladsorbent properties duringexploitation. Samples from previous study are characterized and their pH PZC values are determined. Provided results are such intriguing since they brought conclusions that those values can be explained by process parameters of the particular sample preparation. Sample marked as Cr_2O_3/Fe_3O_4/EVer have lowest pH PZC value (4.75) and sample marked as $MnFe_2O_4$/EVer highest pH PZC value (7.47). Another study in this paper showed that pH PZC value could be easily increased or decreased by simple base or acid treatment, respectfully. As expected, samples treated with bases or prepared in alkali medium have greater adsorption capacity towards cation species, up to 20 % more than base material in the case $MnFe_2O_4$/EVer.

Keywords: adjusting pH PZC, nickel adsorption, expanded vermiculite, ferrites.

INTRODUCTION

One of the most promising methods that can be used in wastewater management is adsorption. Adsorption process is simple, inexpensive and widely applicable. However, adsorbent preparation and adsorption management is more challenging task, since it is recommended to lead the water purification on optimal conditions with paying attention on techno economical parameters.

THEORY AND EXPERIMENTAL

Point of zero charge (PZC) is defined as pH value of the solution which make the solid sample surface zero or isoelectric charged. This parameter should be as less as possible dependable of solution activity. For this reason, all the methods which are used in determining PZC value, execute particular measurements in at least three values of ionic activity. The simplest way for determining PZC is by measuring dependence of final vs initial pH value of the isotonic solutions in the selected pH range [1]. PZC value determined on such method is usually marked as pH PZC and it corresponds to middle of the plateaus where the final pH is almost not changing. Engineers which work on adsorbent development agree that adsorption should be managed on pH values lower than pH PZC of adsorbent if the species which should be adsorbed are negatively charged and vice versa. However, sometimes pH value of polluted samples couldn't be modified or pH adapting is much expensive, for that reason it is needed to prepare adsorbent which is characterized with particular pH PZC value. Another study of Milonjic et al. [2] showed that pH PZC of natural magnetite may be decreased by simple hydrochloric acid treatment. The results from this study are obtained spontaneously, so aim of this paper is to publish to science public the results and conclusions of this study, which can help researchers to prepare optimal adsorbent with targeted pH PZC value.

EXPERIMENTAL SECTION

Samples, used in this study are provided from our previous study [3]beside samples which are subject of this research, there were used further chemicals: potassium hydroxide (Merck Darmstadt, p.a.), nitric acid (ZorkaSabac, 63 mas %), potassium nitrate (Alkaloid Skopje, p.a.), citric acid (Merck Darmstadt, 99.5 mas %) sodium acetate (Lach-NerKiffisia, 98 mas %), nickel nitrate (Merck Darmstadt, 99,999 mas %) and deionized water (DW), (18 MΩ cm).

In order to determine PZC aqueous solutions of potassium nitrate with concentrations of 0.001 M, 0.01 M and 0.1 M were prepared. Each solution present single array that consists of 11 samples (50.0 ml of the solution placed into 250 ml Erlenmeyer flasks) with the same ionic strength but different pH values. Nitric acid and potassium hydroxide were used for adjusting the pH of solutions. Each set with the same ionic strength had 11 samples with the pH value from 2.00 to 12.00. The pH values were measured using Metrohm 781 pH/Ion Meter. Afterwards 100.0 mg of each

adsorbent was added into thus prepared solutions. All those Erlenmeyer flasks were put on a shakerHeidolphUnimax 1010 for 24 hours at 210 rpm. After 24 h pH value of every single solution in all the three arrays was measured and values of initial and final pH value of every single array were used as data for determining PZC of EV, as well as EV modifications. Original method for determining pH PZC can be found in work of Milonjic et al. [1].

Another study is done to check possibility of adjusting pH PZC value after synthesis. All the samples obtained in our previous study [3] were treated with aqueous solution of citric acid and sodium acetate both solutions with the same concentration (0.1 M) for 30 minutes, 1 hour, 2 hours, 4 hours and 24 hours. Volume of the acid and sodium acetate was set on 50 ml and mass of the adsorbent sample was 100 mg. Shaker used for this study was the same as one used for pH PZC determining. After treatment, samples are washed with DW and their pH PZC were determined in the same manner as done after synthesis.

Adsorption experiments were done in a batch system by mixing 1 mg of treated and untreated of each sample in 7500 µl of adsorbate. Constant temperature (298 K) needed for isothermal experiments was provided by water bath. All experiments were done in triplicate for attenuating the measurement uncertainty. According to solubility product of $Ni(OH)_2$ [4], pH value at which the precipitation will occur at 10 mg l^{-1} concentrations is at pH=9. Adsorption experimentswere performed at pH values bellow samples pH_{PZC} which was highest for $MnFe_2O_4$/EVer (7.50). The pH values of the adsorbates were set by using diluted aqueous solutions of KOH and HNO_3. Standardization of the initial nickel solution (1000 mg l^{-1}) was done following the method Accu Standard 1000 ppm. Nickel concentrations were measured by AAS method on Perkin Elmer PinAAcle 900T.The adsorption capacity was calculated using the following equation (1):

$$q = \frac{(C_i - C_e) \times V}{m} \quad (1)$$

RESULTS AND DISCUSSION

It is previously mentioned that pH PZC is determined as theplateaus of the final vs initial pH value. On the Figures 1 – 5 are presented functional dependence of final vs initial pH value for base material EVer and its four modifications: Fe_3O_4/EVer, $MnFe_2O_4$/EVer, $CoFe_2O_4$/EVer and Cr_2O_3/Fe_3O_4/EVer.

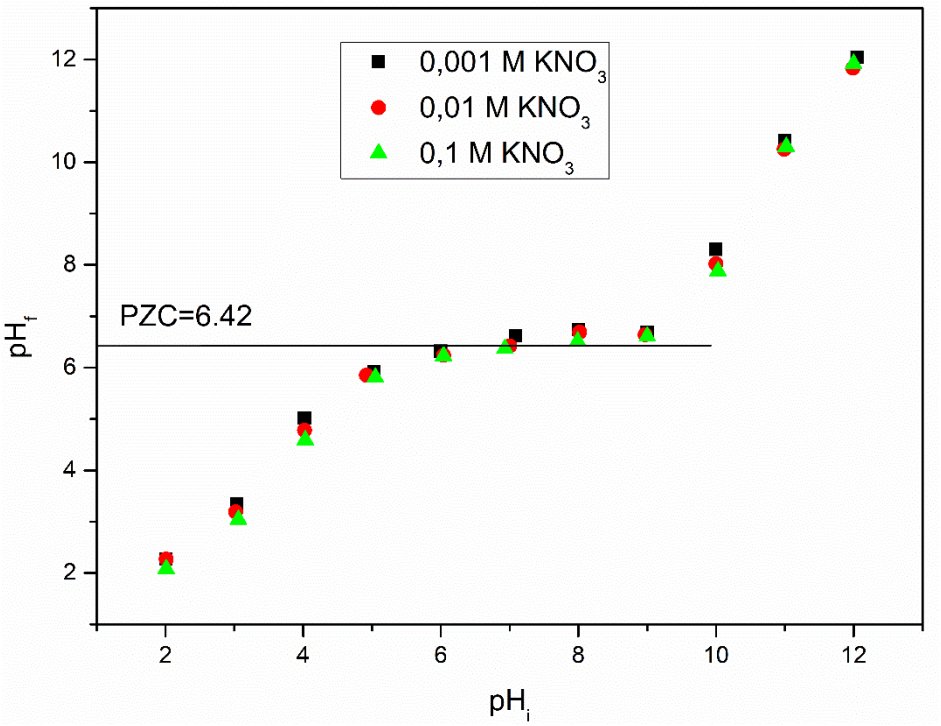

Figure 1: *Relation of initial versus final pH of EVer from the method of pH PZC determination*

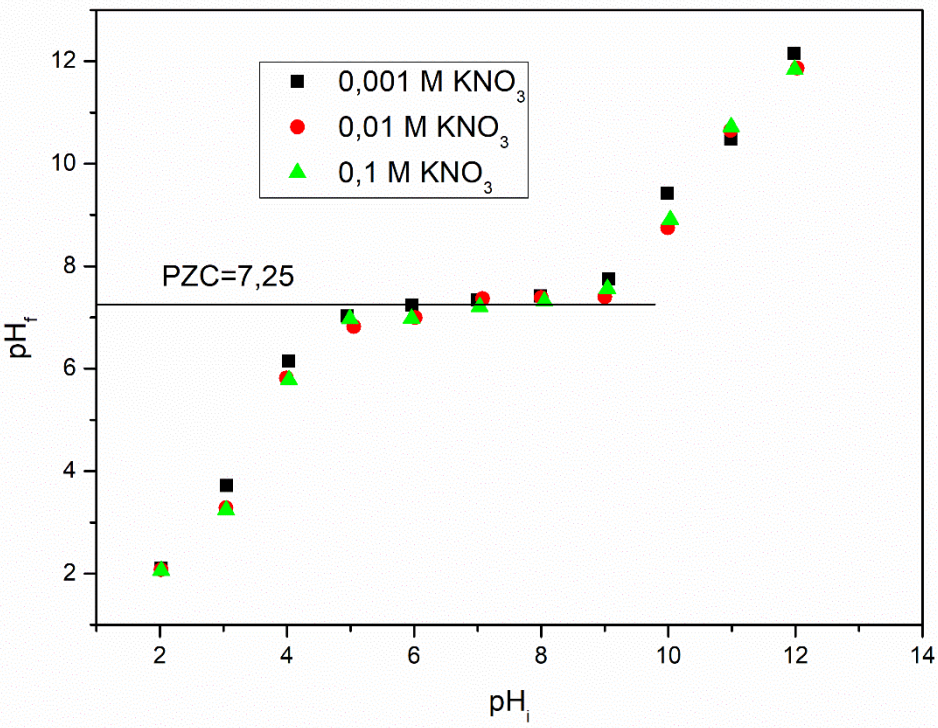

Figure 2: *Relation of initial versus final pH of Fe_3O_4/EVer from the method of pH PZC determination*

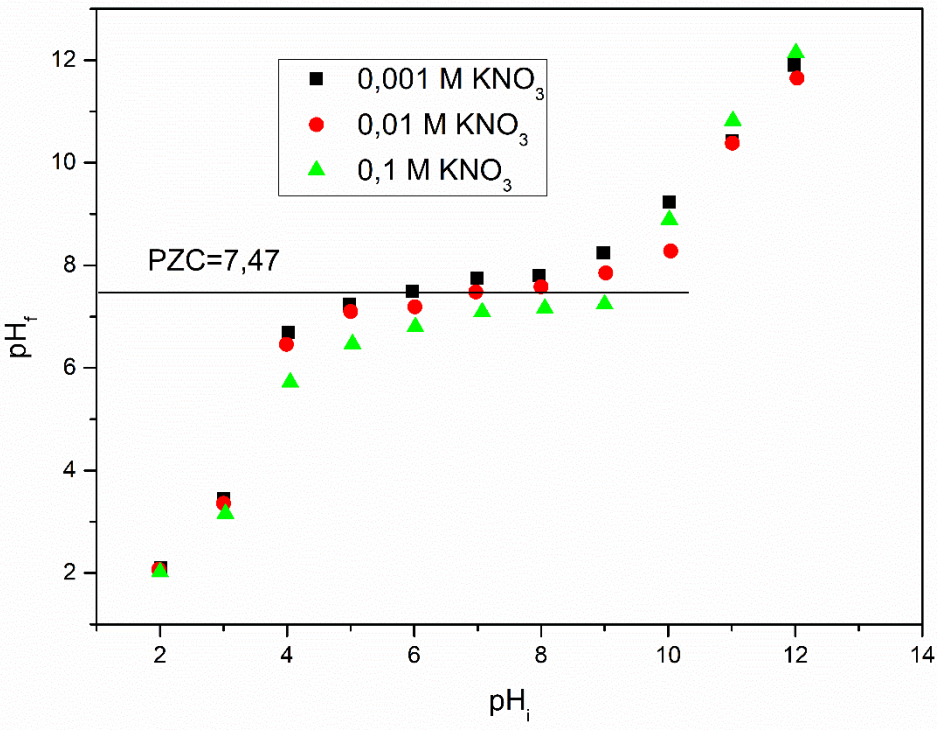

Figure 3: *Relation of initial versus final pH of $MnFe_2O_4$/EVer from the method of pH PZC determination*

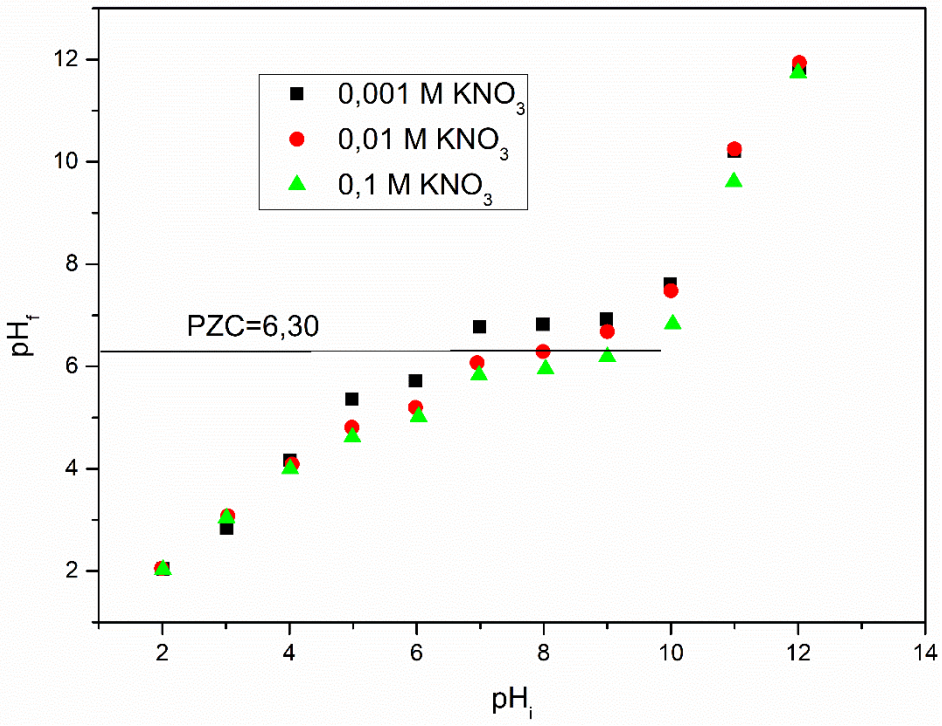

Figure 4: *Relation of initial versus final pH of $CoFe_2O_4$/EVer from the method of pH PZC determination*

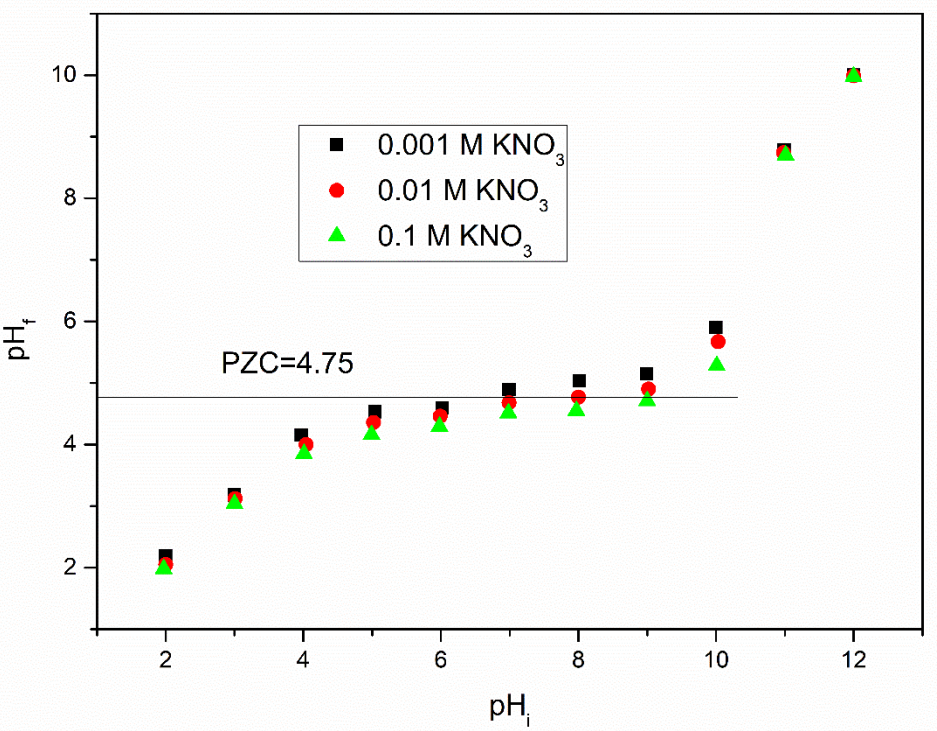

Figure 5: *Relation of initial versus final pH of Cr_2O_3/Fe_3O_4/EVer from the method of pHPZC determination*

Such results may be explained by the acidity and alkalinity of the reagents used for particular ferrite deposition. In the case of Fe_3O_4/EVer it was potassium hydroxide, which were present for less than one hour in solution. On the other hand, $MnFe_2O_4$/EVer was prepared in the hydrothermal process using sodium acetate as reagent medium, resulting in greater pH PZC increase, this substance wasn't an reagent, so it didn't spend during the deposition process. Sample marked as $CoFe_2O_4$/EVer had lower pH PZC than starting material due to presence of weak acids during the deposition process: Co^{2+} - ion and $SO_{2(aq)}$, while the sample Cr_2O_3/Fe_3O_4/EVer had the lowest pH PZC thanks to presence of citric acid which was used as a ligand of Fe^{3+} and Cr^{3+} ions.

Results from pH PZC adjusting study is showed as a table for better transparency and simplicity for comparing results.

Table 1: *Results of the pH PZC adjusting using 0.1 M citric acid on EVer and its modifications*

Sample	Acid treatment period/ h				
	0.5	1	2	4	24
EVer	6.31	6.20	6.10	6.05	6.00
Fe_3O_4/EVer	7.02	6.80	6.54	6.29	6.17
$MnFe_2O_4$/EVer	7.13	6.85	6.58	6.27	6.15
$CoFe_2O_4$/EVer	6.17	6.14	6.11	6.05	5.98
Cr_2O_3/Fe_3O_4/EVer	4.75	4.74	4.74	4.73	4.72

As it can be seen all the samples had much lower values of pH PZC after citric acid treatment except Cr_2O_3/Fe_3O_4/EVer whose pH PZC drop to 4.72.Using the literature data [4] it can be calculated pH value of 0.1 M citric acid, calculated pH value of 0.1 M citric acid is 3.70. Such hydrogen ion activity was high enough to adjust pH PZC value to presented values. Also it can be seen that pH PZC drop for the $MnFe_2O_4$/EVer was the steepest, this results come from the structure of the $MnFe_2O_4$ particles, their size and distance between 2:1 layers in this sample (all the results are presented in the previous study[3]).

Table 2: *Results of the pH PZC adjusting using 0.1 M sodium acetate on EVer and its modifications*

Sample	Base treatment period/ h				
	0.5	1	2	4	24
EVer	6.48	6.56	6.67	6.80	6.90
Fe_3O_4/EVer	7.27	7.31	7.34	7.36	7.38
$MnFe_2O_4$/EVer	7.48	7.48	7.49	7.50	7.51
$CoFe_2O_4$/EVer	6.54	6.69	6.83	6.95	7.02
Cr_2O_3/Fe_3O_4/EVer	5.00	5.22	5.37	5.59	5.70

Results from Table 2 clearly show that Cr_2O_3/Fe_3O_4/EVer had the biggest increase of pH PZC considering its initial pH PZC value of only 4.75. It should be noted that this sample act as a donor of hydronium ions to acetate anion which resulted in production of acetic acid and acetic buffer. Treating the sample EVer with sodium acetate, made its surface weakly acid, which is caused by weak donation of hydronium ions to acetate anion. Acetate anion increased pH PZC of other samples to values of weak bases. The lowest increase of pH PZC was on the sample $MnFe_2O_4$/EVer, this sample was prepared in the basic medium of the same substance so its pH PZC value didn't increase as in the case of other samples. Decrease and increase trend of pH PZC value for $CoFe_2O_4$/EVer was similar which shows that this sample can easily be treated and prepared for exploitation.

However, the most important adsorbent parameter is adsorption capacity. This study was done only for start samples and samples treated after 24 h with citric acid and sodium acetate. In Table 3 are listed the calculated adsorption capacities for nickel ions on all sample before and after acid and salt treatment.

Table 3: *Nickel adsorption capacities for EV and its modifications before and after 24 h citric acid and sodium acetate treatment (0.1 M aqueous solutions):*

Sample	Before treatment	Acid treatment	Base treatment
	q/ mg g^{-1}		
EVer	17.925	17.214	18.103
Fe_3O_4/EVer	12.347	11.877	13.002
$MnFe_2O_4$/EVer	20.250	18.991	21.602
$CoFe_2O_4$/EVer	18.381	17.688	18.927
Cr_2O_3/Fe_3O_4/EVer	15.340	15.230	15.869

Increased nickel adsorption capacities is notable for all samples after sodium acetate treatment, however highest increase was on the sample $MnFe_2O_4$/EVer. These results are explainable with composition of each sample interlayer, distance between the layers and yield of ferrite particles.

CONCLUSIONS

Results from this study pointed the possibility of adjusting pH PZC to desirable value. Also, as expected, nickel adsorption capacities of all samples are increased with simple increasement of pH PZC value. It is possible that samples treated with acid would show greater adsorption parameters for adsorbing some anion species, such as arsenates, selenates or chromates.

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