

The Statistical Significant of Adsorbents for Effective Zn (II) Ions Removal

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Abstract—The adsorption efficiency of various adsorbents for the removal of Zn(II) ions from the waste printing developer was studied in laboratory batch mode. The maximum adsorption efficiency of 94.1% was achieved with unfired clay pellets size ($d \approx 15$ mm). The obtained values of adsorption efficiency was subjected to the independent-samples t test in order to investigate the statistically significant differences of the investigated adsorbents for the effective removal of Zn(II) ions from the waste printing developer. The most statistically significant differences of adsorption efficiencies for Zn(II) ions removal were obtained between unfired clay pellets (size $d \approx 15$ mm) and activated carbon ($|t|=6.909$), natural zeolite ($|t|=10.380$), mixture of activated carbon and natural zeolite ($|t|=9.865$), bentonite ($|t|=6.159$), fired clay ($|t|=6.641$), fired clay pellets (size $d \approx 5$ mm) ($|t|=6.678$), fired clay pellets (size $d \approx 8$ mm) ($|t|=3.422$), respectively.

Keywords—Adsorbent, adsorption efficiency, statistical analysis, zinc ion.

I. INTRODUCTION

ENVIRONMENTAL pollution by toxic metals arises from industrial sources, agricultural effluents, and waste disposal [1]. Wastewaters generated from the printing activities mainly include zinc and copper ions as pollutant. Zinc was intensively studied as pollutants, due to their persistence and toxicity. Also, Zn(II) ion, as a priority pollutants proposed by Environmental Protection Agency (EPA), gives rise to serious poisoning cases. Therefore, the removal of Zn(II) ions from waste flow is an important in the field of water purification. Zinc can be treated by using various physicochemical methods: adsorption, ion exchange, chemical settling, and reverse osmosis. Among them, adsorption receives considerable interest with the high efficiency in heavy metal removal [2]. Due to the different adsorbents, such as clay [2], [3], bentonite [4], zeolite, and activated carbon [5], [6], are in the usage.

The objective of this study was to investigate the statistically significant differences of various adsorbents for

the removal of Zn (II) ions from the waste printing developer as well as to indicate the most effective adsorbent for the purification process.

II. MATERIALS AND METHODS

A. Adsorbate

The sample of waste printing developer was taken from an offset printing facility, Novi Sad (Serbia).

B. Adsorbent

Activated carbon (AC), natural zeolite (NZ), their mixture (AC+NZ), bentonite (B), fired clay (C), modified fired clay with polyethylene glycol addition (MC), fired clay pellets (size $d_1 \approx 5$ mm and $d_2 \approx 8$ mm noted as FCP5 and FCP8, respectively), and unfired clay pellets (size $d_3 \approx 15$ mm, UFCP15) were chosen for the adsorption process.

C. Adsorption Experiment

The adsorption experiments of Zn(II) ions onto the adsorbents were carried out in laboratory batch mode by shaking 0.04 - 0.24 g of each adsorbent with 25 mL of waste printing developer at a shaking speed of 160 rpm and shaking time of 30/60/75/90 min for UFCP15; FCP8; FCP5, MC, C and B; and AC+NZ, NZ, and AC, respectively. At the end of the predetermined time intervals, the solutions are centrifuged for 10 minutes at 3000 rpm and then filtered through a quantitative filter paper (Advantec, grade 5C). The equilibrated Zn(II) ion concentrations were determined in the acidified filtrate (cc HNO_3) by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) method using a PerkinElmer Elan 5000 mass spectrometer.

The adsorption efficiencies of used adsorbents are calculated based on (1):

$$E = \frac{100V(C_0 - C_e)}{VC_0} \quad (1)$$

where E is the adsorption efficiency (%), C_0 is the initial concentration of Zn(II) ions (mg/L), C_e is the equilibrium concentration of Zn(II) ions (mg/L), and V is the volume of waste printing developer (L) [3], [6].

Adsorbents, AC, NZ, AC+NZ, B, C, MC, FCP5, FCP8, and UFCP15, achieved the maximum adsorption efficiency of 73.6, 63.2, 55.6, 89.8, 90.6, 93.5, 90.7, 92.8, and 94.1%, respectively.

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D. Statistical Analysis

In order to investigate the statistically significant differences of used adsorbents for the removal Zn (II) ions from the waste printing developer the independent-samples *t* test was used.

The independent-samples *t* test is the simplest and the most widely used test in statistics. It compares the average values of a characteristic measured on a continuous scale between two subgroups of a variable. The difference of average values of small independent samples is calculated based on (2) [7]:

$$t = \frac{\bar{x}_1 - \bar{x}_2}{\sqrt{\left(\frac{(n_1 - 1)sd_1^2 + (n_2 - 1)sd_2^2}{n_1 + n_2 - 2} \right) \cdot \left(\frac{1}{n_1} + \frac{1}{n_2} \right)}} \quad (2)$$

where \bar{x}_1 is an average value of sample 1, \bar{x}_2 is an average value of sample 2, n_1 is a number of subject in sample 1, n_2 is a number of subject in sample 2, sd_1^2 is a variance of sample 1, and sd_2^2 is a variance of sample 2.

III. RESULTS AND DISCUSSION

The increase of adsorption efficiency with increasing of the adsorbents dosage was observed, Fig. 1, due to the increasing of the surface negative charge and decreasing of the electrostatic potential near the solid surface that favors adsorbent-adsorbate interactions.

Comparison of *E* values indicates that adsorbent UFCP15 achieved the highest adsorption efficiency of 94.1% in the removal of Zn (II) ions from the waste printing developer.

The obtained *E* values were subjected to the independent-samples *t* test in order to evaluate whether the target

adsorbents differ in adsorption efficiency of Zn(II) ions removal. The results of *t* test are represented in Table I.

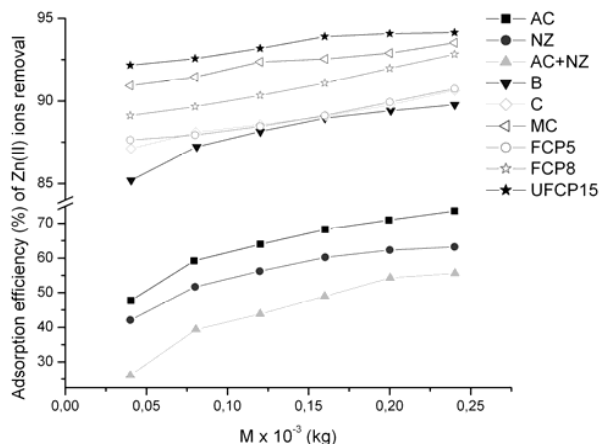


Fig. 1 The adsorption efficiency of used adsorbents for Zn(II) ions removal

The obtained $|t|$ -values were compared with a two-tailed $t_{critical}$ value. The significance level (α) and the degrees of freedom (df) were 0.05 and 10, respectively.

Evidently, bolded $|t|$ -values for AC and NZ, NZ and AC+NZ, B and C, B and FCP5, C and FCP5, MC and FCP8, as well as MC and UFCP15 indicate that the null hypothesis ($H_0: \mu_1 = \mu_2$) is accepted ($|t|$ -values are less than $t_{critical}$ of 2.228, Table I). Thus, it can be concluded that there was no statistically significant difference in the adsorption efficiency of the mentioned adsorbent combinations for the removal of Zn(II) ions from the waste printing developer.

TABLE I
 $|t|$ -VALUES FOR TARGET ADSORBENTS

Adsorbent	$ t $ -value								
	Adsorbent								
	AC	NZ	AC+NZ	B	C	MC	FCP5	FCP8	UFCP15
AC	-	1.445	2.969	5.614	5.831	6.653	5.856	6.275	6.909
NZ		-	1.849	8.784	9.080	10.071	9.114	9.589	10.380
AC+NZ			-	8.728	8.928	9.642	8.950	9.307	9.865
B				-	0.799	4.781	0.908	2.745	6.159
C					-	4.859	0.118	2.324	6.641
MC						-	4.844	1.912	1.863
FCP5							-	2.252	6.678
FCP8								-	3.422
UFCP15									-

Bold indicate $|t|$ -values that are less than $t_{critical}$

All other adsorbent combinations, Table I, show the opposite statistical behaviour. In these cases $|t|$ -values were higher than $t_{critical}$ indicating that the null hypothesis is rejected and the alternative hypothesis ($H_1: \mu_1 \neq \mu_2$) is accepted. The observed adsorbent combinations indicated the statistically significant difference in the adsorption efficiency for the removal of Zn (II) ions from the waste printing developer.

Certainly, the most significant differences in adsorption efficiencies of Zn(II) ions removal were obtained comparing UFCP15 and AC, NZ, AC+NZ, B, C, FCP5, FCP8, respectively. The higher $|t|$ -values indicate that UFCP15 statistically contribute to the effective Zn(II) ions removal from the waste printing developer. The reason for that is the

composition of unfired clay pellets and their shorter adsorption uptake time (30 min).

IV. CONCLUSION

The adsorption efficiency of various adsorbents was tested in order to investigate their statistically significant differences for the removal of Zn (II) ions from the waste printing developer. The independent-samples t test was performed on the obtained data set (values of adsorption efficiency). The results indicated that between AC and NZ, NZ and AC+NZ, B and C, B and FCP5, C and FCP5, MC and FCP8, as well as MC and UFCP15 was no statistically significant difference in the adsorption efficiency of Zn(II) ions removal. Whereas, statistical combination of UFCP15 with AC, NZ, AC+NZ, B, C, FCP5, and FCP8 shown the opposite statistical behaviour i.e. $|t|$ -values for these adsorbent combinations were higher than $t_{critical}$. Therefore, the results indicated that unfired clay pellets are the most statistically significant and effective adsorbent for Zn(II) ions removal from the waste printing developer.

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