



Removal of Fe^{2+} , Zn^{2+} and Mn^{2+} from the mining wastewater by lemon peel waste

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Abstract: This study is aimed to evaluate the possibility of lemon peel, as an agro-industrial waste, to remove Fe^{2+} , Zn^{2+} and Mn^{2+} from single aqueous solutions and mining wastewater. For this purpose, the influence of various parameters: sorption time, initial pH solution, initial metal ion concentration and a dose of sorbent on the sorption process were studied in batch experiments. The experimental equilibrium data have been analysed utilizing linearized forms of Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms. The Langmuir isotherm provided the best theoretical correlation of the experimental equilibrium data for Fe^{2+} , Zn^{2+} and Mn^{2+} , with the maximum sorption capacities of 4.40, 5.03 and 4.52 mg g^{-1} , respectively. The percentage of targeted ions removal from single aqueous solutions was 92.9 % (Zn^{2+}), 84.5 % (Fe^{2+}) and 78.2 % (Mn^{2+}). Regarding the sorption capability of lemon peel in mining wastewater, the maximum removal of Fe^{2+} , Zn^{2+} and Mn^{2+} from mining wastewater was 49.62, 33.97 and 9.11 %, respectively. In addition, the potential reusability of the lemon peel as sorbent was investigated through desorption study in 0.1M of CH_3COO_4 , HCl and HNO_3 solution. The highest rate of desorption was achieved in 0.1 M HCl solution, reached a value of 55.19 % for Mn^{2+} and 37.24 % for Zn^{2+} , while for Fe^{2+} the highest value of 25.82 % was achieved in 0.1M HNO_3 solution.

Keywords: sorption; citrus peel; biosorbent; wastewater.

INTRODUCTION

Mining wastewater is one of the largest sources of environmental contamination, because it contains large amounts of dissolved heavy metals that are persistent in aqueous systems and can be harmful for living organisms in rivers.^{1,2}

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In order to protect the environment and preserve the supply of drinking water, it is necessary to purify wastewater before releasing it into the environment.

Adsorption method has been increasingly used for removal of the heavy metals ions from water systems, because of its efficiency, simplicity, low operational costs and full availability.³ Activated carbon is one of the most commonly used and highly effective adsorbent for the removal of heavy metal ions. However, due to its high price and low regeneration rate it has limited application,³ so the quest for cheaper sorbent continues.

The most common problems in selecting a suitable sorbent are related to the favourable price, full availability of sorbent and high selectivity of sorbent to remove heavy metal ions from water systems. By appropriate modification methods, properties of the sorbents can be improved, but in that case, the price of the entire process of purification of polluted water is increased. In order to solve these problems, research is focused on finding natural and cheap materials that can be used. In recent years, a great deal of interest has been focused on the use of agro-industrial waste as sorbents.⁴⁻⁷ Large quantities of waste materials, such as peel, generated during industrial processing of lemons, have an unfavourable environmental impact. Waste lemon peel is mainly deposited in landfills, where can potentially cause soil and local water pollution and in some cases can lead to uncontrolled methane production.⁸⁻¹⁰ On the other side, lemon peel has a high quantity of pectin that contains hydroxyl and carboxylic groups that can bond the divalent cations (heavy metals).^{11,12} Due to their global availability, physical stability and high pectin content, lemon waste has the potential to be used as a cheap sorbent for the removal of divalent cations.

In our previous work,¹³ we confirmed that unmodified lemon peel could efficiently remove the copper ions from the aqueous system and mining wastewater of "RTB Bor". In this paper, we extend the previous studies on adsorption processes of unmodified lemon peel, investigating the sorption ability toward other common metal ions from mining wastewater of "RTB Bor" (Fe^{2+} , Zn^{2+} and Mn^{2+}). Namely, the sorption property of unmodified lemon in single aqueous solutions and in mining wastewater that contains a mix of all metal ions was investigated.

EXPERIMENTAL

Sorbent material

Lemon taken from a nearby supermarket was washed with tap water to remove impurities and soluble substances. The lemon peel separated from the edible part was grounded in a mill and washed with deionized water until the disappearance of yellow colour. Afterward, the peel was dried in an oven at 105 ± 2 °C until constant weight, to remove the moisture completely. Dried lemon peel was additionally ground to obtain powdered sorbent.

Characterization of sorbent

In order to get the detailed insight into the chemical composition of a sorbent, the content of ash, protein, fat, cellulose, acidic and basic functional group of lemon peel were analysed.

Determination of the ash content was carried out in the prescribed method according to Standard Methods¹⁴ in two repetitions, and the results are shown as the mean value.

The protein determination of lemon peel was performed by the Kjeldahl method. The nitrogen content was determined by the oxidation of the sample to water, carbon dioxide and ammonia, which was then converted to boric acid solution by distillation. The amount of ammonia converted to the distillate was determined by titration.¹⁵

The determination of the fat content of the lemon peel was done gravimetrically. First, the destruction of the sample was carried out by digestion of 5 g of raw lemon peel with 60 mL of concentrated HCl and 100 mL of distilled water in a period time of 20 min. The sample was filtrated and washed with hot distilled water until the negative reaction to chlorides. Thereafter the sample was dried in an oven at 103 °C, after which extraction was carried out in the Soxhlet's extractor for 3 h in 150 mL of diethyl ether. Upon complete extraction, the content was evaporated into a rotary evaporator and dried at 103 °C until constant weight. Fat content expressed in percentages was calculated as the difference in mass before and after the extraction divided by the initial mass of the lemon peel.

The cellulose content was determined by a gravimetric method. Namely, 1 g of lemon peel was boiled with stirring in 25 mL aliquots of a mixture containing 75 mL of 75 % acetic acid, 5 mL of nitric acid and 2 g of trichloroacetic acid. After half an hour, a sample was filtrated and washed 3 times with the remaining mixture, then with diethyl ether and finally with acetone. After filtration, the filter paper with the sample was dried at 103 °C to the constant weight. The content of cellulose is determined from the difference in the mass of the filter itself and filter with sample after filtration.

To quantify the acidic and basic oxygen functional groups on the sorbent surface, the Boehm titration method was used. The number of acidic sites were calculated under the assumption that NaOH neutralizes carboxylic, phenolic and lactonic groups; Na₂CO₃ neutralizes carboxylic and lactonic groups; and NaHCO₃ neutralizes only carboxylic groups.¹⁶ Experimentally, 0.5 g of lemon peel sorbent was shaken for 24 h in 50 mL of 0.1 N solutions of three different bases (NaHCO₃, Na₂CO₃ and NaOH). Afterward, the suspensions were filtrated and 10 mL of aliquots from each filtrate were used for titration. The aliquot of NaOH was directly titrated with 0.1 N HCl. The other two aliquots (Na₂CO₃ and NaHCO₃) were acidified by the addition of 0.1 N HCl to ensure complete neutralization of bases and then back titration was performed with 0.1 N NaOH. An analogous procedure determined the basic groups in the sorbent. 0.5 g of the sample was immersed in 0.1 N HCl for 24 h and afterward, the direct titration with 0.1 N NaOH was used. Titration was followed pH-metrically and the endpoint was pH 7. It is essential to underline that nitrogen was passed through all aliquots for 15 min before and during titration to avoid carbonic acid formation with CO₂ from the air.

The content of acidic and basic functional groups was determined using the following Eq. (1) for direct titration,¹⁷ and Eq. (2) for back titration:

$$c_{\text{functional group}} = \frac{c_i V_i - c_t V_t (V_i / V_a)}{m_{\text{sorbent}}} \quad (1)$$

$$c_{\text{functional group}} = \frac{(n_{\text{HCl}} / n_i) c_i V_i - (c_{\text{HCl}} V_{\text{HCl}} - c_t V_t) (V_i / V_a)}{m_{\text{sorbent}}} \quad (2)$$

where c_i is initial concentration of the base or acid in mol L⁻¹, V_i is the initial volume of base or acid in L, n_i is the number of moles of initial base or acid, V_a is the aliquots from each filtrate used for titration in L, C_{HCl} is concentration of acid added for acidification of base in mol L⁻¹, V_{HCl} is the volume of acid added for acidification of base in L, n_{HCl} is the number of moles of added HCl to the aliquot before titration, c_t is concentration of titrant in mol L⁻¹, V_t is the volume of titrant in L and m_{sorbent} is mass of sorbent in g.

Batch sorption experiments

The efficiency of Fe²⁺, Zn²⁺ and Mn²⁺ removal by lemon peel were tested in single aqueous solutions and multicomponent mining wastewater. Single solutions of investigated Fe²⁺, Zn²⁺ and Mn²⁺ at different concentrations and pH were prepared by dissolving their sulphate salts in deionised water. The pH values of the solution were adjusted by adding 0.1 M HNO₃ and 0.1 M NaOH solutions. Batch sorption experiments were performed at room temperature (25 °C), immersing a certain mass of a sorbent in 50 mL of the test solution and stirred on a magnetic stirrer at 1200 rpm for specific contact time. Afterward, the solutions were filtrated through a membrane filter (pore size 0.45 μm). To find the optimum conditions for the sorption process, the mass of sorbent was varied from 0.10 to 1.0 g, the contact time from 15 to 120 min, the initial pH of the solution from 2 to 5 and the initial metal ion concentration from 10 to 200 mg L⁻¹. The concentrations of all investigated metal ions were measured by ICP-OES. Each experiment was repeated three times under the same controlled conditions and the mean values are reported. The reproducibility and the relative standard deviation were of the order ±2 and ±3 %, respectively.

The data obtained in batch studies were used to calculate the amount of sorbed metal ions and the efficiency of sorption. The sorption capacity was calculated according to the following equation:

$$q_e = (C_0 - C_e) \frac{V}{m} \quad (3)$$

where q_e is the amount of sorbed metal ions per unit mass of sorbent in mg g⁻¹, C_0 is the initial concentration of metal ions in mg L⁻¹, C_e is the final or equilibrium concentration of metal ions in solution in mg L⁻¹, V is volume of the used metal ions solution in L and m is mass of the sorbent in g.

The efficiency of sorption shows the percentage of metal ions removal and is calculated as follows:

$$\text{ADS, \%} = 100 \frac{C_0 - C_e}{C_0} \quad (4)$$

Linearized forms of Langmuir, Freundlich, Dubinin–Radushkevich and Temkin isotherms, presented in the Supplementary material to this paper, were used to study the distribution of selected heavy metal ions between solution and the sorbent under equilibrium conditions.

Desorption studies

In order to determine the potential reusability of the lemon peel sorbent, the desorption process was performed. Desorption was investigated with three different solutions: 0.1 M CH₃COOH; 0.1 M HNO₃ and 0.1 M HCl (mass of metal ion loaded sorbent 1.0 g; a volume of solution 50 mL; duration of process 15 min). Desorption efficiency was calculated according to the following equation:

$$DES, \% = 100 \frac{C_d}{C_{ads}} \quad (5)$$

where C_d is a concentration of metal ions in solution after desorption process in mg L^{-1} and C_{ads} initial concentration of metal ions onto sorbent in mg L^{-1} .

RESULTS AND DISCUSSION

Characterization of lemon peel

The content of ash, fat, protein and cellulose in lemon peel sorbent are presented in Table I. The chemical composition of lemon peel shown in Table I is not complete, only the components that are important for the analysis of lemon peel as a sorbent are given. Hence, the total content of hemicellulose, lignin, flavonoids and sugars was not evaluated.

TABLE I. Chemical composition of lemon peel waste

Component	Content, %
Ash	1.17
Fat	0.31
Protein	2.00
Cellulose	9.70

The behaviour of sorbents depends mostly on its chemical composition. Cellulose is the least reactive substance in lignocellulosic materials, and therefore, the higher the content of the cellulose in the material, its reactivity is lower. The content of cellulose in lemon peel waste is below 10 %, thus it should not significantly diminish the sorption capabilities of lemon peel. On the other side, proteins are biomolecules composed of amino acids, where $-\text{NH}_2$ and COO^- groups have an affinity for reaction with metal ions, thus accelerating the sorption capabilities of lemon peel. However, in this case, the content of protein is significantly low, around 2 %. The values of ash, protein and cellulose content obtained in this work are similar to the values published in the literature for the lemon peel.¹⁸

Boehm titration was applied to further identify the quantity of the acidic and basic functional groups on the lemon peel surface. According to the results shown in Table II, the acidic groups are more presented than basic groups, leading to the conclusion that the surface of the lemon peel is acidic. Unlike orange peel that contains total acidic groups 2.47 mmol g^{-1} and base groups 0.5 mmol g^{-1} ,¹⁹ lemon peel contains a larger amount of acidic and base groups, which makes it a more suitable sorbent in acidic medium.

TABLE II. Boehm titration results for lemon peel; concentration, mmol g^{-1}

Carboxylic groups	Lactonic groups	Phenolic groups	Total acidic groups	Total basic groups	Total groups
0.9	1.6	1.4	3.9	1.05	4.95

Sorption results

The influence of dose of sorbent. The influence of the lemon peel dose on the sorption process of the selected heavy metal ions from the aqueous solution is shown in Fig. 1. These data were obtained by varying the dose of lemon peel from 0.10 to 1.0 g, while the other working parameters were constant. The percentage of removal of Zn^{2+} , Fe^{2+} and Mn^{2+} significantly increases with the rise of the lemon peel dose, while sorption capacity decreases. The increased removal of metal ions from aqueous solutions is expected since higher sorbent dose generates more active sites for metal ions binding. On the other hand, the decrease in sorption capacity is a result of the unsaturation of all active sites. The maximum percentage of removal corresponds to a mass of 1.0 g of lemon peel and is 92.97 % for Zn^{2+} , 84.50 % for Fe^{2+} and 78.20 % for Mn^{2+} . Bohli *et al.*²⁰ showed that the degree of removal of metal ions is directly dependent on the ionic radius. The higher the ionic radius, the higher is its tendency for binding. In this case, Zn^{2+} has the highest ionic radius (74 pm), so it is expected to be more bounded on lemon peel sorbent than Fe^{2+} (ionic radius 70 pm) and Mn^{2+} (ionic radius 70 pm).

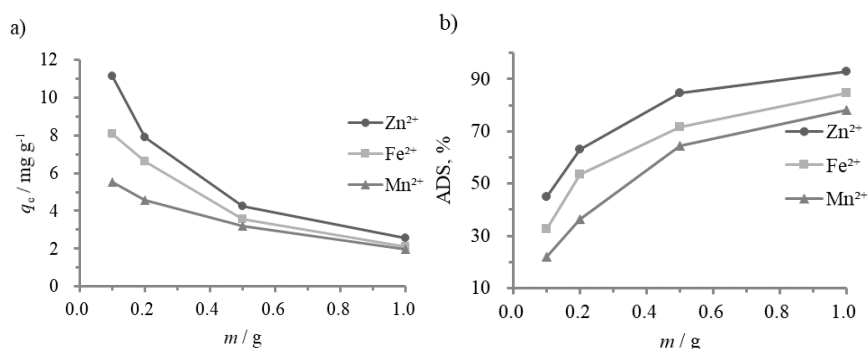


Fig. 1. Influence of the mass of lemon peel on: a) sorption capacity and b) sorption percentage for removal of metal ions. The initial concentration of the metal ion solution was 50 mg L^{-1} , contact time 15 min and temperature $25 \text{ }^\circ\text{C}$.

The influence of contact time of sorbent. The influence of contact time on the sorption of metal ions by a lemon peel is presented in Fig. 2. The percentage of Zn^{2+} , Fe^{2+} and Mn^{2+} removal and the sorption capacity decrease with the increase of the contact time from 15 min to 2 h. Since maximum percent of metal ions removal was achieved within 15 min (for Zn^{2+} 92.9 %, Fe^{2+} 84.5 % and Mn^{2+} 78.2 %), this contact time period was selected for all further experiments. Due to fast achieved equilibrium sorption state, it was not possible to perform sorption kinetic experiments and to completely confirm the sorption mechanism. It is important to underline that the sorption equilibrium by a lemon peel is achieved within 15 min of contact time, which is significantly shorter time for sorption in comparison to the other fruit peels adsorbent reported in the literature.

For example, the equilibrium time for removal of zinc ions by musk melon peel was 70 min,²¹ by carbonated orange peel was 60 min,²² by kiwi, banana and tangerine peel was 60 min,²³ and by durian peel was 4 h.²⁴ Adsorption of iron ions by banana peel was 24 h,²⁵ by pomegranate peel was 40 min,²⁶ whereas adsorption of manganese ions by modified banana peel was 1 h.²⁷ The fast sorption of metal ions achieved in this work has a great practical significance, as it allows water purification in a short period, which contributes to the greater economy and efficiency of the purification process.

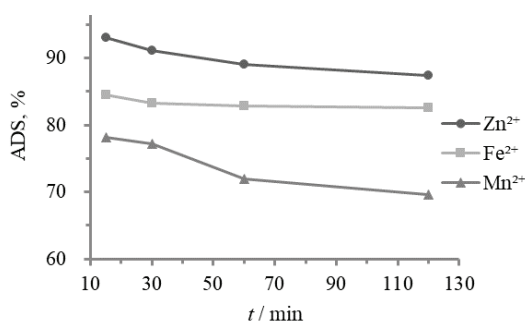


Fig. 2. Influence of contact time on metal ions removal. The mass of sorbent was 1.0 g, the initial concentration of metal ions solution was 50 mg L⁻¹ and temperature 25 °C.

Effect of solution pH on Fe²⁺, Zn²⁺ and Mn²⁺ sorption. The influence of the initial pH of the solution on the sorption properties of lemon peel was tested for each selected metal ion separately in the pH range between 2 and 5. The experiments were not performed at higher pH value due to the precipitation of targeted metal ions (for Fe²⁺ at pH 5.35, for Zn²⁺ at pH 7.4 and for Mn²⁺ at pH 7.5). The sorption percentage of lemon peel plotted *versus* the initial pH is shown in Fig. 3. The removal of Fe²⁺, Zn²⁺ and Mn²⁺ is very low at highly acidic conditions (pH 2), whereas an increase of the pH from 2 to 3 leads to a significant rise in the percentage of removal of all tested metal ions. The maximum ADS value is reached at pH 4 for Zn²⁺ (92.9 %), Fe²⁺ (84.5 %) and Mn²⁺ (78.2 %), while with a further increase of pH the ADS % value slightly decreases. The same trend was observed regarding sorption capacity with an increase in pH value. The influence of the pH can be explained based on the pK_a value of the

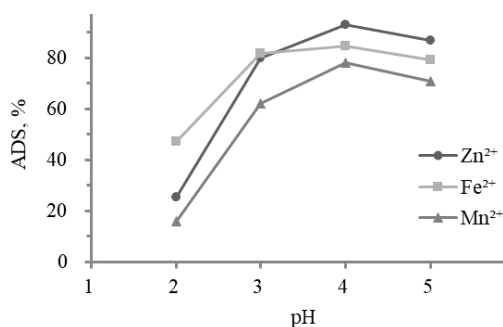


Fig. 3. Initial pH effect on the sorption of Fe²⁺, Zn²⁺ and Mn²⁺ on lemon peel. The mass of sorbent was 1.0 g, the initial concentration of metal ions solution was 50 mg L⁻¹ and temperature 25 °C.

carboxyl group, which is in the range of 3.38–4.1,²⁸ depending on the degree of esterification carboxyl groups present in pectin component of lemon peel.²⁹

At low pH ($\text{pH} < \text{pKa}$), the protonation of carboxyl groups occurs. Simultaneously with decreasing pH, the competition between hydrogen ions and metal cations for active sites on the surface of the sorbent is increased. The effect of this phenomenon is the reduction of the ion sorption capacity. Although at a higher pH ($\text{pH} > \text{pKa}$) the surface of the sorbent has a negative charge as a result of the ionization of the acid carboxyl groups and the increase of sorption capacity would be expected, a slight decrease of sorption efficiency at pH 5 was obtained. However, it was observed that during the sorption process the pH of metal ion solution is not constant and that lemon peel lowered the pH of metal ions solutions from 5 to 4–4.3, which could be possible explanation for unusual trend.

Adsorption isotherms

In order to evaluate the effect of initial metal ion concentration on sorption capability of lemon peel, the batch experiments were carried out immersing 1.0 g of lemon peel into 50 mL of tested ions solution at different initial concentrations (10, 30, 50, 70, 100, 150 and 200 mg L^{-1}). The solutions were stirred for 15 min at 1200 rpm with a magnetic stirrer. The experimental equilibrium data have been analyzed by the use of linear forms of Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms. The obtained values for the isotherm constants and the coefficients of determination (R^2) are reported in Table III.

TABLE III. Isotherm parameters for Zn^{2+} , Fe^{2+} and Mn^{2+} sorption onto the lemon peel

Model	Parameters	Zn^{2+}	Fe^{2+}	Mn^{2+}
Langmuir	R^2	0.98	0.99	0.97
	$q_m / \text{mg g}^{-1}$	5.03	4.40	4.52
	$K_l / \text{L mg}^{-1}$	0.26	0.11	0.07
Freundlich	R^2	0.96	0.95	0.87
	n	1.92	2.08	2.31
	$K_f / \text{mg}^{1-1/n} \text{g}^{-1} \text{L}^{1/n}$	0.98	0.59	0.55
Dubinin–Radushkevich	R^2	0.72	0.79	0.93
	$\beta / \text{mol}^2 \text{kJ}^{-2}$	20.0	80.0	2.00
	$q_m / \text{mg g}^{-1}$	3.90	2.90	2.86
	$E / \text{kJ mol}^{-1}$	1.58	0.79	0.50
Temkin	R^2	0.93	0.98	0.97
	B	1.37	0.92	0.72
	$K_T / \text{L g}^{-1}$	1.91	1.15	1.35
	$\Delta H / \text{J mol}^{-1}$	-1812	-2680	-3442

The Langmuir isotherm is found to provide the best theoretical correlation of the experimental equilibrium data for Fe^{2+} , Zn^{2+} and Mn^{2+} , with the maximum sorption capacities of 4.40, 5.03 and 4.52 mg g^{-1} , respectively. This indicates the monolayer sorption of metal ions on the lemon peel. These results agree with the

literature data for the interaction between citrus pectin and cations Fe^{2+} and Zn^{2+} , best described by the Langmuir isotherm.^{28,30} Moreover, an analysis of the experimental equilibrium data for metal ions resulted in an equally good correlation with Temkin isotherm, which is correlated to chemisorption of sorbate onto the sorbent.³¹ This model also assumes that the energy of the sorption of molecules decreases linearly with the surface coverage due to sorbent–sorbate interaction.

Comparing results in this work with data from the literature presented in Table IV, it can be observed that the lemon peel studied in this work shows good sorption capacity for Zn^{2+} , Fe^{2+} and Mn^{2+} at acidic pH conditions.

TABLE IV. Comparisons of the lemon peel sorption capacity (q_{max} / mg g⁻¹) with other sorbents from the literature

Sorbent	Ion			Reference
	Zn ²⁺	Fe ²⁺	Mn ²⁺	
White rice husk ash	/	/	15.20	32
Pomegranate peel carbon	/	18.52	/	26
Rice husk ash	/	6.21	3.02	33
Untreated banana peel	/	/	2.86	34
Untreated coffee residues	4.40	/	/	35
Banana peel	5.80	/	/	36
Orange peel	5.25	/	/	36
Natura sugarcane bagasse	0.06	0.83	0.46	37
Lemon peel	5.03	4.40	4.52	This study

Desorption results

The efficient desorption of metal-loaded sorbent is an essential fact for the possibility to re-use the lemon peel as sorbent again. Obtained results presented in Table V show that 0.1 M HCl found to be the most effective medium for the desorption of Mn^{2+} and Zn^{2+} , reaching values of 55.19 and 37.24 %, respectively. For the desorption of Fe^{2+} , the most effective medium is 0.1 M HNO_3 , with a desorption rate of 25.82 %. However, the degree of desorption is not high enough to allow the lemon peel to be re-used for new adsorption.

TABLE V. Desorption efficiency (DES / %) of metal ions from lemon peel in different media

Medium	Ion		
	Zn ²⁺	Fe ²⁺	Mn ²⁺
0.1 M CH_3COOH	20.66	18.86	40.38
0.1 M HNO_3	34.33	25.82	35.50
0.1 M HCl	37.24	21.88	55.19

Use of sorbent in wastewater

For the investigation of lemon peel efficiency in the real system, the copper mining industrial wastewater was used from the Bor mining, in Serbia. Mining wastewater is characterized by a low pH value (pH 2.5–3) and a high concentration of more than one metal. This wastewater contains high concentrations of Zn^{2+} (47 mg L^{-1}), Fe^{2+} (15 mg L^{-1}) and Mn^{2+} (66 mg L^{-1}). When more than one metal is present in the sorption system, the evaluation of sorption results, their interpretations and representation become more complicated. To investigate the applicability of lemon peel in a real system, batch experiments were carried out by using 3 different doses of sorbent (1, 2 and 3 g) mixed for 15 min in 50 mL of wastewater solution at speed rate 1200 rpm. Because the present study is aimed to find a simple and inexpensive way for the purification of wastewater from Zn^{2+} , Fe^{2+} and Mn^{2+} by lemon peel, it was decided not to adjust the pH of the mining wastewater. Based on the results shown in the Table VI, it can be concluded that lemon peel is more effective in removing Fe^{2+} (49.62 %) and Zn^{2+} (33.97 %). A low rate of metal ions removal in real wastewater indicates that pre-treatment of water is needed in order to increase the efficiency of the sorbent.

Table VI. Removal of metal ions from mining wastewater (*ADS* / %)

Mass of sorbent, g	Ion		
	Zn^{2+}	Fe^{2+}	Mn^{2+}
1	9.13	43.67	1.91
2	16.09	38.83	3.47
3	33.97	49.62	9.11

CONCLUSIONS

In this paper, the conversion of lemon peel waste into useful sorbent against three types of water pollutants (Fe^{2+} , Zn^{2+} and Mn^{2+}) was investigated. The prominent acidic groups on the surface of lemon peel played a significant role in binding the metal ions from aqueous and mining wastewater solutions. It was found that removal of targeted ions from aqueous single solutions was 92.9 (Zn^{2+}), 84.5 (Fe^{2+}) and 78.2 % (Mn^{2+}), whereas its efficiency in mining wastewater was 49.62 (Fe^{2+}), 33.97 (Zn^{2+}) and 9.11 % (Mn^{2+}). Although lemon peel appeared to be efficient for removal of divalent cations from single aqueous solutions, further studies should be carried out, in terms of pre-treatment of mining wastewater and potential modification of lemon peel surface, in order to increase its practical adsorption efficiency in multicomponent real wastewater systems.

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ИЗВОД
УКЛАЊАЊЕ Fe^{2+} , Zn^{2+} и Mn^{2+} ИЗ ОТПАДНЕ ВОДЕ РУДНИКА КОРИШЋЕЊЕМ
ОТПАДНЕ КОРЕ ЛИМУНА

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Циљ овог рада је да се испита могућност коришћења коре лимуна, као агро-индустријског отпада, за уклањање Fe^{2+} , Zn^{2+} и Mn^{2+} из њихових водених раствора и из отпадне воде рудника. С тим у вези испитиван је утицај различитих параметара: времена сорпције, почетне рН вредности раствора, почетне концентрације јона метала и дозе сорбента на процес сорпције. Експериментално добијени подаци у сорпционој равнотежи анализирани су користећи линеарне облике Ленгмирове, Фројндлихове, Темкинова и Дубинин–Радуш-кевичеве изотерме. Ленгмирова изотерма је приказала најбољу теоријску корелацију са експерименталним подацима за Fe^{2+} , Zn^{2+} и Mn^{2+} са максималним сорпционим капацитетима 4,40, 5,03 и 4,52 mg g^{-1} , редом. Процент уклањања циљаних јона из њихових водених раствора је 92,9 (Zn^{2+}), 84,5 (Fe^{2+}) и 78,2 % (Mn^{2+}). Испитивањем сорпционе способности лимунове коре у рударским отпадним водама, добијено је да је максимално уклањање Fe^{2+} , Zn^{2+} и Mn^{2+} из отпадне воде рудника 49,62, 33,97 и 9,11 %, редом. Поред тога, могућност поновне употребе коре лимуна као сорбента је испитана проучавањем десорпције у 0,1 М раствору CH_3COO_4 , HCl и HNO_3 . Највећа стопа десорпције постигнута је у 0,1 М раствору HCl , и достигла је вредност од 55,19 % за Mn^{2+} и 37,24 % за Zn^{2+} , док је за Fe^{2+} највећа вредност од 25,82 % постигнута у 0,1 М раствору HNO_3 .

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REFERENCES

1. E. Malkoc, *J. Hazard. Mater.* **137** (2006) 899 (<https://doi.org/10.1016/j.jhazmat.2006.03.004>)
2. S. E. Bailey, T. J. Olin, R. M. Bricka, D. D. Adrian, *Water Res.* **33** (1999) 2469 ([https://doi.org/10.1016/S0043-1354\(98\)00475-8](https://doi.org/10.1016/S0043-1354(98)00475-8))
3. U. Kumar, *Sci. Res. Essay* **1** (2006) 33 (<https://doi.org/10.5958/j.0974-4487.11.1.001>)
4. T. Ahmad, M. Danish, *J. Environ. Manage.* **206** (2018) 330 (<https://doi.org/10.1016/j.jenvman.2017.10.061>)
5. Š. Abdić, M. Memić, E. Šabanović, J. Sulejmanović, S. Begić, *Int. J. Environ. Sci. Technol.* **15** (2018) 2511 (<https://doi.org/10.1007/s13762-018-1645-7>)
6. A. Bhatnagar, M. Sillanpää, A. Witek-Krowiak, *Chem. Eng. J.* **270** (2015) 244 (<https://doi.org/10.1016/J.CEJ.2015.01.135>)
7. C. K. Jain, D. S. Malik, A. K. Yadav, *Environ. Process.* (2016) 495 (<https://doi.org/10.1007/s40710-016-0143-5>)
8. D. A. Zema, P. S. Calabrò, A. Folino, V. Tamburino, G. Zappia, S. M. Zimbone, *Waste Manage.* **80** (2018) 252 (<https://doi.org/10.1016/j.wasman.2018.09.024>)
9. M. E. Magare, N. Sahu, G. S. Kanade, C. S. Chanotiya, S. T. Thul, *Waste Biomass Valorization* **11** (2020) 165 (<https://doi.org/10.1007/s12649-018-0385-8>)
10. D. Mamma, P. Christakopoulos, *Waste Biomass Valorization* **5** (2013) 529 (<https://doi.org/10.1007/s12649-013-9250-y>)
11. Y. N. Mata, M. L. Blázquez, A. Ballester, F. González, J. A. Muñoz, *Chem. Eng. J.* **150** (2009) 289 (<https://doi.org/10.1016/j.cej.2009.01.001>)
12. E. F. Lessa, A. L. Medina, A. S. Ribeiro, A. R. Fajardo, *Arab. J. Chem.* **13** (2020) 709 (<https://doi.org/10.1016/j.arabjc.2017.07.011>)

13. S. Meseldžija, J. Petrovic, A. Onjia, T. Volkov-Husovic, A. Nestic, N. Vukelic, *J. Ind. Eng. Chem.* **75** (2019) (<https://doi.org/10.1016/j.jiec.2019.03.031>)
14. *APHA Standard Methods for the Examination of Water and Wastewater*, 17th ed., American Public Health Association, Washington DC, 1989
15. S. S. Nielsen, *Food Analysis Laboratory Manual*, Springer International Publishing, Cham, 2017 (<https://doi.org/10.1007/978-3-319-44127-6>)
16. H. P. Boehm, *Carbon N. Y.* **32** (1994) 759 ([https://doi.org/10.1016/0008-6223\(94\)90031-0](https://doi.org/10.1016/0008-6223(94)90031-0))
17. S. L. Goertzen, K. D. Thériault, A. M. Oickle, A. C. Tarasuk, H. A. Andreas, *Carbon N. Y.* **48** (2010) 1252 (<https://doi.org/10.1016/j.carbon.2009.11.050>)
18. M. Masmoudi, S. Besbes, M. Chaabouni, C. Robert, *Carbohydr. Polym.* **74** (2008) 185 (<https://doi.org/10.1016/j.carbpol.2008.02.003>)
19. X. Li, Y. Tang, X. Cao, D. Lu, F. Luo, W. Shao, *Colloids Surfaces, A* **317** (2008) 512 (<https://doi.org/10.1016/j.colsurfa.2007.11.031>)
20. T. Bohli, I. Villaescusa, A. Ouedern, *J. Chem. Eng. Process Technol.* **04** (2013) (<https://doi.org/10.4172/2157-7048.1000158>)
21. K. Anitha, R. J. Rinu Isah, *Int. J. Pure Appl. Math.* **116** (2017) 91 (<https://acadpubl.eu/jsi/2017-116-13-22/articles/13/16.pdf>)
22. E. Bernard, A. Jimoh, *Int. J. Eng. Appl. Sci.* **4** (2013) 95 ([http://eaas-journal.org/survey/userfiles/files/v4i212%20chemical%20engineering\(1\).pdf](http://eaas-journal.org/survey/userfiles/files/v4i212%20chemical%20engineering(1).pdf))
23. K. M. Al-Qahtani, *J. Taibah Univ. Sci.* **10** (2016) 700 (<https://doi.org/10.1016/j.jtusci.2015.09.001>)
24. M. Ngabura, S. A. Hussain, W. A. W. A. Ghani, M. S. Jami, Y. P. Tan, *J. Environ. Chem. Eng.* **6** (2018) 2528 (<https://doi.org/10.1016/j.jece.2018.03.052>)
25. S. L. Shrestha, *Int. J. Appl. Sci. Biotechnol.* **6** (2018) 137 (<https://doi.org/10.3126/ijasbt.v6i2.20423>)
26. M. R. Moghadam, N. Nasirizadeh, Z. Dashti, E. Babanezhad, *Int. J. Ind. Chem.* **4** (2013) 19 (<https://doi.org/10.1186/2228-5547-4-19>)
27. A. Ali, *Environ. Nanotechnology, Monit. Manage.* **7** (2017) 57 (<https://doi.org/10.1016/j.enmm.2016.12.004>)
28. M. Celus, C. Kyomugasho, Z. J. Kermani, K. Roggen, A. M. Van Loey, T. Grauwet, M. E. Hendrickx, *Food Hydrocoll.* **73** (2017) 101 (<https://doi.org/10.1016/j.foodhyd.2017.06.021>)
29. J. N. BeMiller, in *Chem. Funct. Pectins*, American Chemical Society, Washington DC, 1986, pp. 2–12 (<https://doi.org/10.1021/bk-1986-0310.ch001>)
30. M. Y. Khotimchenko, E. A. Kolenchenko, Y. S. Khotimchenko, *J. Colloid Interface Sci.* **323** (2008) 216 (<https://doi.org/10.1016/j.jcis.2008.04.013>)
31. K. Biswas, S. K. Saha, U. C. Ghosh, *Ind. Eng. Chem. Res.* **46** (2007) 5346 (<https://doi.org/10.1021/ie061401b>)
32. M. P. Tavlieva, S. D. Genieva, V. G. Georgieva, L. T. Vlaev, *J. Mol. Liq.* **211** (2015) 938 (<https://doi.org/10.1016/j.molliq.2015.08.015>)
33. Y. Zhang, J. Zhao, Z. Jiang, D. Shan, Y. Lu, *Biomed Res. Int.* **2014** (2014) 1 (<https://doi.org/10.1155/2014/973095>)
34. A. Ali, K. Saeed, *Desalin. Water Treat.* (2014) 37 (<https://doi.org/10.1080/19443994.2013.876669>)
35. C. Wu, C. Kuo, S. Guan, *Pol. J. Environ. Stud.* **24** (2015) 761 (<https://doi.org/10.15244/pjoes/31222>)
36. G. Annadurai, R. S. Juang, D. J. Lee, *Water Sci. Technol.* **47** (2003) 185 (<https://doi.org/10.2166/wst.2003.0049>)
37. P. A. Milani, K. B. Debs, G. Labuto, E. N. V. M. Carrilho, *Environ. Sci. Pollut. Res.* **25** (2018) 35895 (<https://doi.org/10.1007/s11356-018-1615-0>).