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Composite materials based on orange and pomegranate peels for Cu (II) and Zn (II) ions extraction

Abstract. The method of obtaining composite materials based on orange (OP) and pomegranate (PP) peels is described. The fruit peels were modified by polyethylene glycol (PEG). Sorption ability of obtained composite materials towards heavy metal ions (Zn and Cu) was studied. The effect of the mass of composite materials and PEG concentration were studied. The optimal concentration of PEG was determined as 0.1%. The maximum removal degree of heavy metals was at 2 and 2.5 g per 100 ml of solution for orange and pomegranate peels respectively. Three different adsorption models were used to describe the sorption process (Langmuir, Freundlich, and BET). The most applicable for the sorption of Zn (II) and Cu (II) ions by both OP and PP is Freundlich theory. Hence, the sorption of Zn (II) and Cu (II) ions by modified peels of orange and pomegranate occurs at a heterogeneous system where the active centers are unevenly filled.
Key words: composite material, orange peel, pomegranate peel, polyethylene glycol, sorption, heavy metal.

Introduction

Thousand tons of fruits are eaten every day around the world. In order of utilization of their peels they can be used as sorbents of heavy metals (HM) from wastewater. In accordance with the WHO (World Health Organization), drinking of low quality water can cause human ailments accounted about 80% of health problems' total amount [1]. Purification of water from various pollutants is currently a relevant task, which requires the application of new approaches as well as environmentally-friendly and resource-saving technologies. All these approaches should give the opportunity to use the purified water in production processes, thus decreasing the consumption of freshwater [2].

Many methods and technologies have been developed for the treatment of wastewater from different types of pollutants, particularly from HM ions. They are electrodialysis, coagulation, reverse osmosis, sedimentation, ion exchange, filtration, flocculation and precipitation [3–6]. However these conventional methods are quite expensive [7]. Among all of the developed methods for the treatment of wastewater, containing HM ions, an important place is taken by sorption methods. They allow to provide the most complete removal of toxicions, especially from solutions with low concentrations [8, 9]. Hence, adsorption is one of the promising methods for purification of wastewater and industrial effluents [10].

Such composite materials based on fruit peels and other plant raw materials are low-cost and effective. Low-cost bioadsorbents are based on using household wastes, such as peels of banana, orange, kiwi, pomegranate, tangerine, tomato, potato and pumpkin, also tea wastes and pineapple [11]. Agricultural wastes are also used in bio-sorption [12]. The wastes of crops are one of the sources that are rich of low-cost sorbents. Agricultural wastes show ability to adsorb toxic heavy metal ions, such as mercury, lead, cadmium, nickel, zinc and chromium. According to investigated works [13], sorbents based on agricultural wastes are effective for removal of cadmium ions.

Such household waste as eggshell is also used as bioadsorbent. In the work devoted to removal of copper and lead ions from water eggshell [14], banana peels and pumpkin were used as bioadsorbents. Yellow passion-fruit shell was used as adsorbent for removal of ions of Cr (III) and Pb (II) from water. The highest removal efficiency was observed at pH = 5 both for chromium and lead. The removal efficiency of Cr (III) ions was about 63% and about 20% for Pb (II) [15].

Banana peel was used as adsorbent to remove Cr (VI) ions from industrial wastewater [16]. The sorption process was carried out at the pH range of 1-9. Maximum Cr (VI) removal was observed at pH = 2, the removal degree reaches more than 95 %. Another work has been provided using banana peel as adsorbent for treatment of wastewater collected from Gelox paints, Kaduna state, Nigeria [17].

A lot of research works were performed using orange peel as an adsorbent for heavy metal ions removal [18-20]. Orange peel along with date palm fibers were used to remove copper (II), lead (II) and arsenic (V) ions from aqueous solutions [21].

A lot of researches have been done using peel of pomegranate [22, 23]. Pomegranate peel was used to adsorb copper, cadmium, nickel and zinc ions [24]. Biosorbent shows the highest adsorption capacity of heavy metals at pH 4.5. Adsorption of copper and cadmium ions represents the highest results, followed by ions of zinc and nickel. Adsorption of Cr (VI) is the lowest at pH 4.5. The maximum removal of copper ions was 0.0677 mmol/g at initial 0.787 mmol/l of the solution.

Thus, an analysis of the literature has shown that composite materials based on orange peel and pomegranate peel are of practical interest for use in the process of sorption of heavy metal ions, but they should be modified to increase the sorption activity. For our knowledge, there is no data on the use of polyethylene glycol (PEG) as a modifier for the preparation of composite materials based on orange peel and pomegranate peel in the literature. The previous studies [25] have shown that PEG can be used as an effective modifier of sorbents based on natural materials. The adsorption activity of PEG-modified OP and PP towards copper (II) and zinc (II) ions was studied in the current work.

Materials and methods

Composite materials preparation

Orange (OP) and pomegranate (PP) peels were collected from local markets and juice-producing shops. At first, peels were washed with distilled water, finely cleaned and left to dry at room temperature. Then the dry peels were mechanically ground till fine powder was obtained.

Obtainment of the composite materials based on the peels was carried out according to two-step procedure: first with a solution of sodium hydroxide (NaOH), then with a solution of polyethylene glycol (PEG).

Obtaining the composite material based on orange peel was carried out according to the following procedure. Orange peel powder weighing 5 g is placed in a glass; 100 ml of an aqueous solution containing 0.1 M NaOH is poured into this glass. Next, the resulting solution with the OP is stirred with a glass rod to prevent lumps, and then continued mixing using magnetic stirrer at 100 rpm for 60 min. The resulting gelatinous solution is left over night. On the next day the process of polymer modification begins. First, solution is rinsed with distilled water until a neutral medium is reached (pH of 6-7). Then the solution is filtered. After that the sorbent remaining on the filter paper is dried and subjected to polymer modification. For this purpose, 100 cm^3 of 0.1 % polyethylene glycol is poured into a glass with a sorbent obtained in the previous step. After 60 minutes of stirring on a mixer, composite material is dried in an oven at 100 °C for 2 hours, then left to dry until completely drying at room temperature. The obtained composite material was ground in order to further study of its characteristics.

The composite material based on pomegranate peel was obtained by the same method as in the case of orange peel.

Adsorption experiments

The following solutions containing heavy metal ions of various concentrations are prepared for the experiment:

– solution of the $CuCl_2 \cdot 2H_2O$ salt with a metal concentration of 10-50 μg/ml;

– solution of $ZnCl_2$ salt with a metal concentration of 10-50 μg/ml.

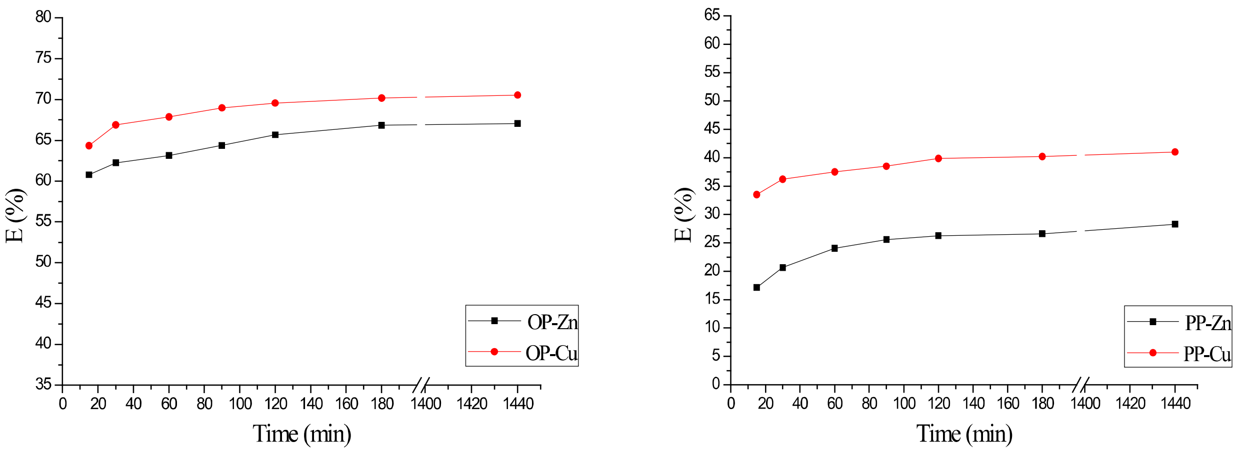
The sorption process was carried out under static conditions with outstirring, at the room temperature equal to T = 298 K.

Sorbent with a mass of 1 g is placed and 100 ml of solution is poured into a measuring cup (flask) with a capacity of 100 cm^3. Furthermore, an aliquot of the solution is taken after a certain period of time and kept at room temperature until equilibrium was established.

Results and discussions

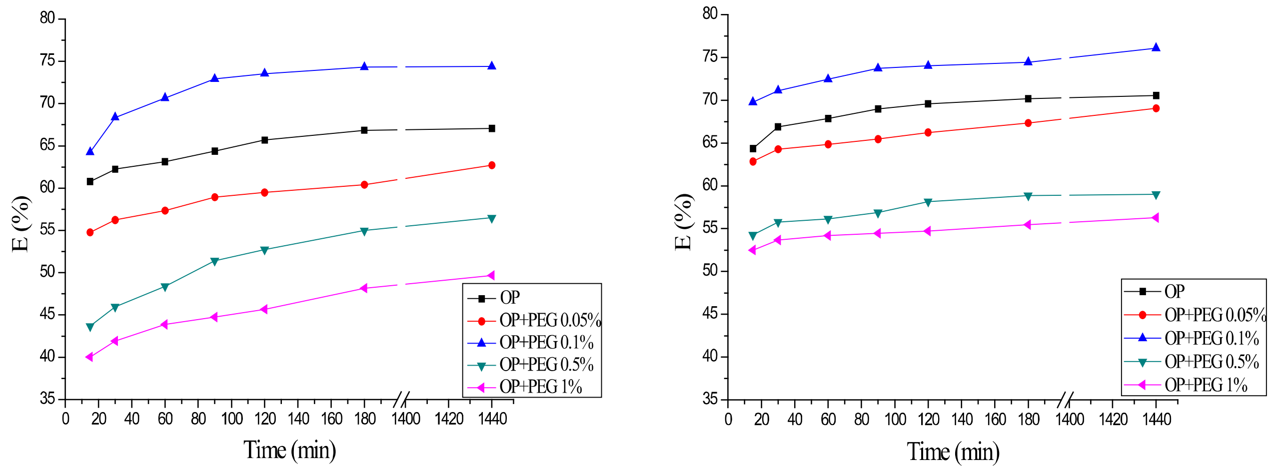
Sorption characteristics of initial and modified composite materials based on orange and pomegranate peels

A comparative analysis sorption activity of the initial materials (orange and pomegranate peels) towards TM ions is represented in Figure 1. It can be seen from the graphs that the peels show different adsorption properties for each metal ion. As can be seen from Figure 1 (a) the removal degree of Zn^{2+} and Cu^{2+} ions reaches about 70 % (67 % and 71 %). The results in Figure 2 (b) show that PP adsorbs copper (II) ions much better than zinc (II) ions (41 % and 28 %). It can be concluded that initial OP has better adsorption properties towards Zn^{2+} and Cu^{2+} ions than initial PP.



a) initial OP b) initial PP

Figure 1 – Dependence of removal degree (%) of Zn^{2+} and Cu^{2+} ions by initial (a) OP and (b) PP on time (T = 298 K, C_{in} = 10 mg/l)



a) Zn^{2+} b) Cu^{2+}

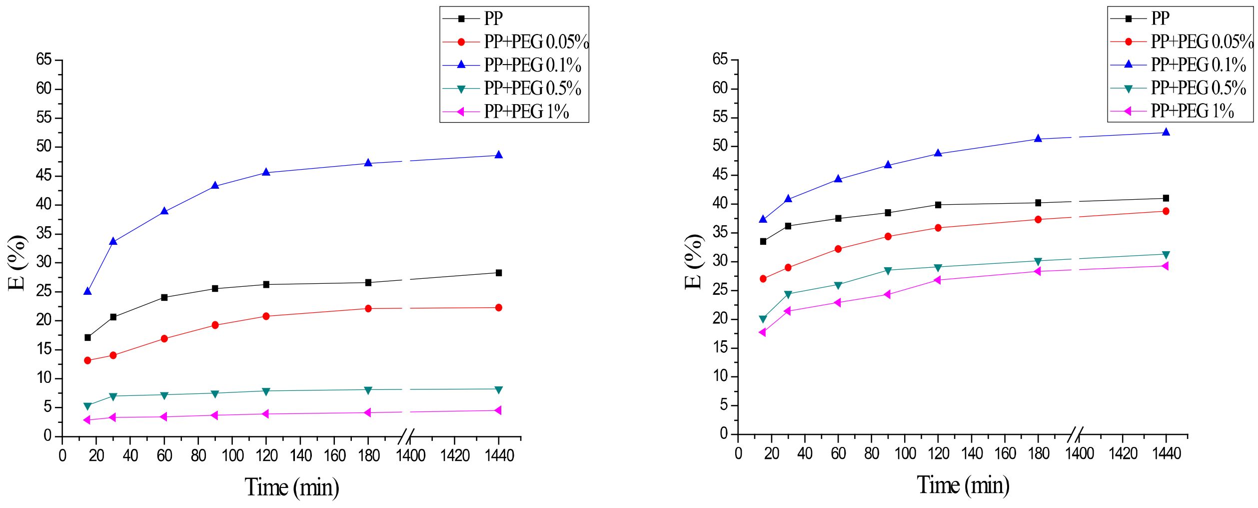
Figure 2 – Dependence of removal degree (%) of (a) Zn^{2+} and (b) Cu^{2+} ions by modified OP at different concentrations of PEG on time (T = 298 K, C_{in} = 10 mg/l)

A comparative analysis of Zn^{2+} and Cu^{2+} ions sorption by modified OP at different concentrations of PEG is represented in Figure 2.

It can be seen from the graphs that the modification of OP by PEG 0.1 % enhanced the sorption ability of the initial peel. The removal degree of Zn^{2+} and Cu^{2+} reaches 74 % and 76 % respectively. However, in both cases, the other concentrations of PEG are not effective compared to the initial OP. It can be concluded that the 0.05 % concentration of PEG is not enough to improve the sorption activity of OP. Meanwhile increasing the concentration of modifier reduces the removal degree of the metal ions due to closing the active centers of peel surface.

Figure 3 represents a comparative analysis of Zn^{2+} and Cu^{2+} ions sorption by modified PP at different concentrations of PEG.

The consequence of sorption activity of modified pomegranate peels are the same as in the case of modified orange peels: 0.1 % > 0.05 % > 0.5 % > 1 %. The removal degree of zinc (II) ions by PP-PEG 0.1 % highly increases in comparison to the initial pomegranate peel (49 %). The lowest removal degree of zinc (II) ions by modified PP (about 5 %) has been observed at the concentration of PEG = 1 %.



a) Zn^{2+} b) Cu^{2+}

Figure 3 – Dependence of removal degree (%) of (a) Zn^{2+} and (b) Cu^{2+} ions on time by modified PP at different concentrations of PEG

The adsorption ability of modified PP towards Cu^{2+} ions are shown in Figure 3 (b). The extraction degree of copper (II) ions by modified polyethylene glycol reaches 52%.

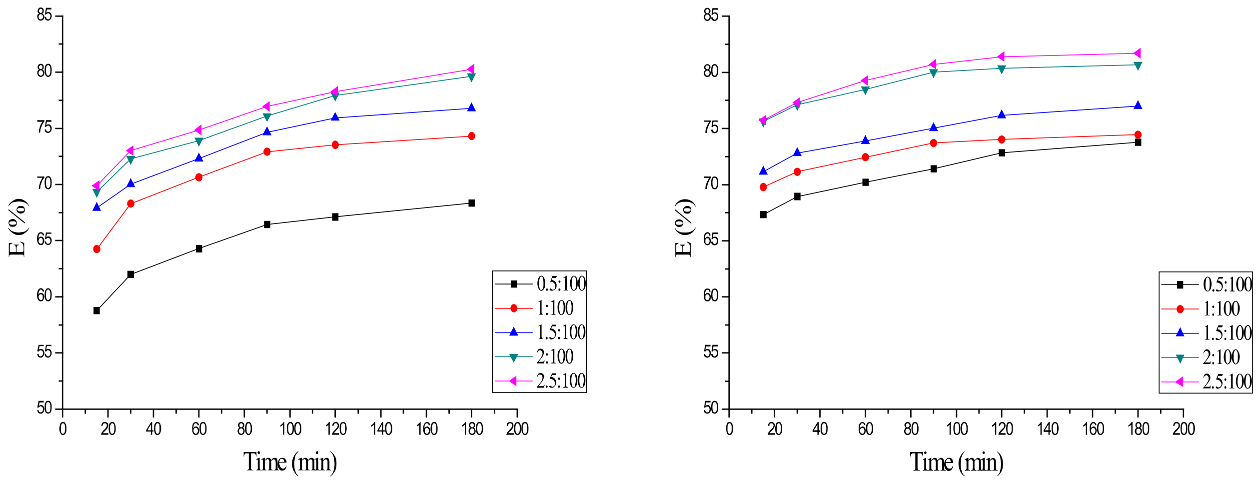
According to the results from the graphs of removal degree dependence of HM ions from time, it can be concluded that the optimal time of equilibrium establishment is 180 minutes. The concentration of the modifier (PEG) equal to 0.1% is optimal to reach the highest removal degree of the metal ions from aqueous solutions, while the lowest results are observed at 1 %. The removal of Zn^{2+} and Cu^{2+} ions by modified OP is about 75 % and the removal degree by modified PP reaches up to 50 %.

Figure 4 shows a comparative analysis of Zn^{2+} and Cu^{2+} ions sorption by modified OP at different masses of sorbents. It can be seen from the graphs that with increasing the mass of the modified orange peel the removal degree of zinc (II) and copper (II) ions also increase. However, there is no considerable difference between the removal degree at 2 g and 2.5 g. Hence, 2 g of modified orange peel was chosen as the optimal mass of sorbent for removal of both Zn^{2+} and Cu^{2+} ions. The removal degree of Zn^{2+} and Cu^{2+} ions by the optimal mass of modified OP reaches about 80 %.

Figure 5 represents a comparative analysis of Zn^{2+} and Cu^{2+} ions sorption by modified PP at different masses of sorbents. In the case of modified pomegranate peel, 2.5 g was the most effective for sorption of zinc (II) and copper (II) ions. The removal degree of Zn^{2+} ions was 80 % and of Cu^{2+} ions was 70 %.

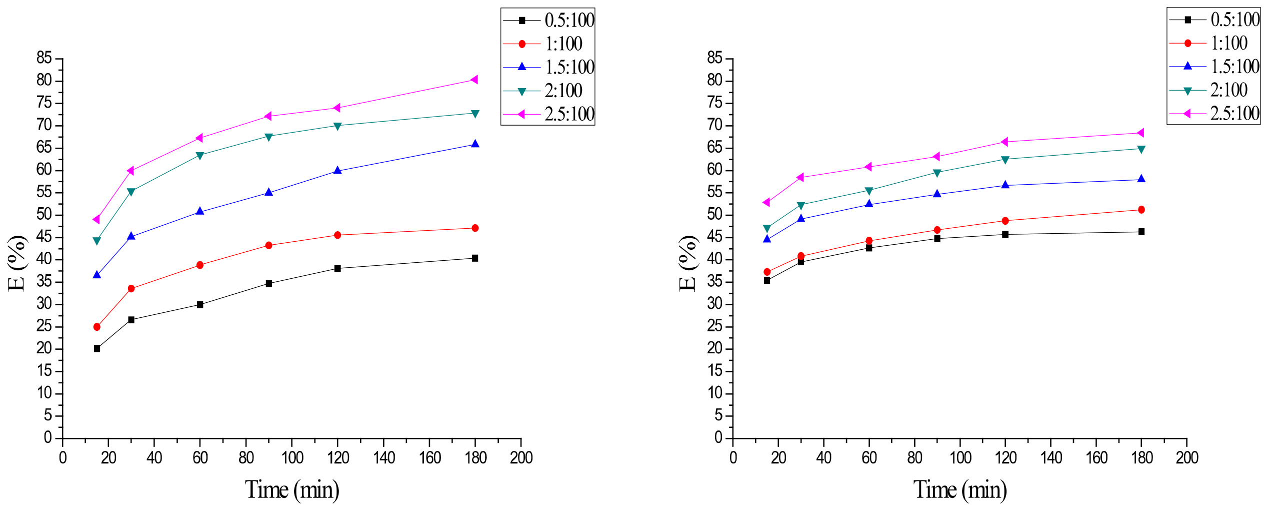
Analysis of isotherms of the sorption process of Zn^{2+} and Cu^{2+} ions from aqueous solutions

Sorption isotherms are of great importance for describing the sorption process. There is no unified model that accurately and fully describe all types of adsorption on different interfaces. Three of the most frequently used models (Langmuir, Freundlich and BET) were used to describe the process of HM ions sorption by the obtained composite materials. Table 1 summarizes the isotherm constants of sorption by composite materials, where K is adsorption equilibrium constant, A_∞ is maximum adsorption, K_{BET} is BET equilibrium constant, K_F and 1/n are Freundlich isotherm constants. According to the data in Table 1, the BET isotherm model does not describe the sorption process. Langmuir theory does not fully describe the process, while the correlation coefficient values of the Freundlich model show better results. Consequently, sorption of Zn^{2+} and Cu^{2+} ions by modified OP and PP occurs at a heterogeneous system with an uneven filling of active centers.



a) Zn^{2+} b) Cu^{2+}

Figure 4 – Dependence of removal degree (%) of (a) Zn^{2+} and (b) Cu^{2+} ions by modified OP at different masses of composite material on time



a) Zn^{2+} b) Cu^{2+}

Figure 5 – Dependence of removal degree (%) of (a) Zn^{2+} and (b) Cu^{2+} ions by modified PP at different masses of composite material on time

Table 1 – Isotherm constants of sorption process by modified peels

Model parameters		OP-PEG		PP-PEG	
		Zn^{2+}	Cu^{2+}	Zn^{2+}	Cu^{2+}
Langmuir theory	K	0.0011	0.0038	0.0156	0.0175
	A_∞, mg/l	26.1780	10.9529	2.0903	1.6150
	R^2	0.0066	0.9436	0.9717	0.9591
Freundlich theory	K_F	0.0501	0.0488	0.0552	0.0499
	1/n	0.8789	0.9157	0.7241	0.7036
	R^2	0.9936	0.9995	0.9976	0.9904
BET theory	K_{BET}	-0.4981	-1.7127	0.8663	0.5803
	A_∞, mg/l	-1.8126	-0.4610	0.8481	0.6141
	R^2	0.2037	0.8642	0.0447	0.1295

Conclusion

The method of obtaining composite materials based on orange and pomegranate peels was developed. Sorbents based on orange and pomegranate peels modified by PEG were used to remove Zn (II) and Cu (II) ions from water and the following conclusions were made:

1. It has been established that the modification of fruit peels by polyethylene glycol (PEG) increases their sorption activity in comparison to the initial peels. The degree of removal of Zn^{2+} and Cu^{2+} ions by the modified orange peel reaches (80 ± 4) %. In case of modified PP the removal degree of Zn^{2+} ions is (80 ± 3) % and of Cu^{2+} ions is (70 ± 5) %.

2. Based on study results the optimal concentration of PEG (0.1 %) and optimal mass of sorbents (2 g for OP+PEG and 2.5 g for PP+PEG) were determined.

3. For the description of process mechanism Langmuir, Freundlich and BET model isotherms were used. The most applicable was Freundlich theory, at which the correlation coefficients were equal to $R^2 = 0.9936$ (OP-PEG-Zn), $R^2 = 0.9995$ (OP-PEG-Cu), $R^2 = 0.9976$ (PP-PEG-Zn) and $R^2 = 0.9904$ (PP-PEG-Cu). It means that the adsorption process goes on a heterogeneous surface with uneven filling and multilayers of adsorbates are formed.

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