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OIL ADSORPTION AND DESORPTION OF BIO-NANOADSORBENTS SYNTHESIZED BASED ON POMEGRANATE PEEL+Fe_3O_4 NANOPARTICLES

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The aim of this study is to evaluate the effectiveness of chemically and biodegradable agricultural waste sorbents and their synthesized bio-nanoadsorbents based on nanoparticles in the remediation of water environments contaminated by oil spills. A new bio-nanocomposite was developed by combining pomegranate peel and Fe_3O_4 magnetic nanoparticles. Based on the adsorption results, it was determined that the adsorption efficiency of 10% pomegranate peel/Fe_3O_4 bio-nanoadsorbent (pH = 7, 0.5 g adsorbent, 78 g/L oil) was 82%, while the adsorption efficiency of the biosorbent obtained with pomegranate peel alone was 52%. The Brunauer–Emmet–Teller (BET) surface area of the synthesized dried bio-nanoadsorbents ranged from 67 m²/g. The results of regeneration experiments showed that the bio-nanoadsorbent could be reused up to 96%. Based on desorption experiments, it was determined that the pomegranate peel/Fe_3O_4 bio-nanoadsorbent desorbed 63.28% of oil with ethanol and 71.9% with acetone. According to the experimental results, it can be argued that the pomegranate peel/Fe_3O_4 bionanocomposite is a new effective adsorbent for the removal of oil and oil products from aqueous solutions and therefore has the potential to be used in environmental pollution cleanup programs.

Keywords: bio-nanoadsorbents, environmental pollution, pomegranate peel, regeneration, desorption, Brunauer–Emmet–Teller (BET)

INTRODUCTION

Discharges of oil and oil products into the aquatic environment are continuously increasing, mainly as a result of industrial activities and technological development [1]. Oil and petroleum products are toxic, even in small quantities in the environment, and therefore can cause many environmental problems when present in the natural environment [1-3]. Several methods have been applied to treat oil-contaminated waters, such as chemical precipitation, adsorption, membrane filtration, and electrochemical treatment. Biosorption has been found to be superior in terms of being economically viable, flexible, simple, and effective compared to other methods [3-5]. The potential of pomegranate peel waste as an adsorbent for the removal of petroleum products from oil-contaminated waters has been widely recognized. In modern literatures, nanomaterials are of great importance in the removal of pollutants due to

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their high surface-to-volume ratio and fast reaction kinetics. The synthesis of Fe_3O_4 superparamagnetic nanoparticles is relatively inexpensive, and Fe_3O_4 superparamagnetic nanoparticles can be applied to the treatment of toxic metals [5,6,7,8,9]. Fe_3O_4 superparamagnetic nanoparticles are not subject to secondary pollution, because elemental iron is environmentally friendly and can be directly applied to contaminated sites. Superparamagnetic nanoparticles are superior to other types of nanoparticles because their magnetic properties allow them to be easily separated from water contaminated with oil and petroleum products [9]. Recently, the biosorption process has been widely used in the treatment of oil-contaminated waters, combined with magnetic separation. The combination of the nanoparticles we used with another sorbent, such as biomass, is more effective because it increases the dispersion by modifying various functional groups [10-13].
In this study, a novel magnetic bio-nanoadsorbent (pomegranate peel/ Fe_3O_4) was synthesized to evaluate its potential for oil removal from aqueous solutions contaminated with oil and petroleum products. The regeneration and reusability of the adsorbent were also studied.

EXPERIMENTAL

In order to study the adsorption properties of the biosorbent containing pomegranate peel (PP) and 10% Fe_3O_4, preliminary tests were conducted at different pH conditions [13-15]. A fixed amount of adsorbent (0.5 g) and an oil concentration of 8.5 g/L (1 ml of oil added to 100 ml of seawater) were used in the experiments. 1 M HCl and 1 M NaOH solutions were used to create acidic and alkaline environments [16].
The adsorption efficiency of both PP and PP+10% Fe_3O_4-containing biosorbents was evaluated by equilibrium studies. The tests were carried out in an 8.5 g/L oil/seawater solution at neutral conditions, room temperature (20 °C) and pH 7. For this purpose, 1.5 g of PP and 0.5 g of PP+10% Fe_3O_4 were used, respectively [16-19].
The adsorption process was carried out with initial oil concentrations varying in the range of 8.5–78 g/L and the final oil concentration was measured for a period of 72 h. Preliminary tests with different adsorbent doses (0.5, 1, 1.5 and 3 g) showed that adsorption reached a nearly steady state at an initial oil concentration of 78 g/L and after 72 h [20,21].
The results show that 1.5 g PP adsorbed approximately 52 g/L (approximately 52%) of oil at the end of 72 h (Figure 1), whereas 0.5 g PP+10% Fe_3O_4 achieved a higher adsorption efficiency with an oil capacity of 64 g/L (approximately 82%) under the same conditions [22,23].

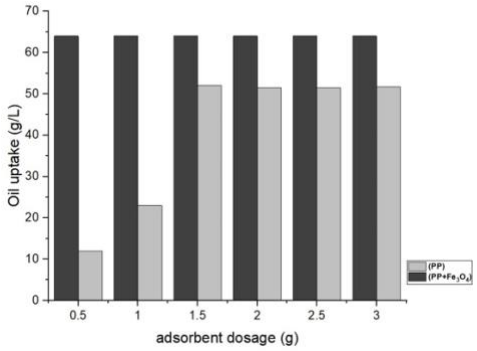

Figure 1. Effect of adsorbent (PP and PP+10%Fe_3O_4) dosage on the oil adsorption. Conditions: 78 g/L as oil initial concentration, room temperature, pH=7 and 72 h.

RESULTS AND DISCUSSION

BET Analysis

BET (Brunauer-Emmett-Teller) analysis for nanoparticles is a gas adsorption method used to measure the specific surface area (m²/g) of nanoparticles, which is important for understanding the properties of nanoparticles [23-25]. The results of BET analysis and pore size distribution (pore volume and diameter) showed that the pomegranate peel/Fe_3O_4 bio-nanoadsorbent had a surface area of 67 m²/g. According to literature data, the BET analysis results for ZnO and Fe_3O_4 nanoparticles vary in the range of 20–80 m²/g. The bio-nanoadsorbent we synthesized has a surface area of 67 m²/g meaning that the material has some porosity and surface activity, but not as a very highly porous material. But it results in a good level of adsorption capacity of the bio-nanoadsorbent [25-26].

Desorption and reuseability

The bionanoadsorbent synthesized based on pomegranate peel + Fe_3O_4 nanoparticles that we use in the purification of oil-contaminated water is washed with a suitable solvent (usually ethanol, hexane, or acetone, depending on its solubility in oil) or by adjusting the pH. The experiment continues with mixing for 10 minutes to desorb the oil [26]. Then, the regenerated bionanadsorbent is washed with distilled water in laboratory conditions and dried in a Muffle furnace (temperature 60 ^{0}C).
The efficiency of desorption is determined as:

$$\mathrm{DE}(\%) = \frac{q_d}{\mathrm{qe}} \times 100$$

q_d = amount of oil desorbed (mg/g)
q_e = amount of oil initially adsorbed (mg/g)

Reusability Performance (R%)
To evaluate the stability of the adsorbent across multiple cycles: [26]

$$\mathrm{R}(\%) = \frac{q_n}{\mathrm{q1}} \times 100$$

- q_n = adsorption capacity in the nth cycle (mg/g)
- q_1 = adsorption capacity in the first cycle (mg/g)

This shows how much adsorption efficiency is retained after several regenerations.

Table 1. Reusability Performance results for bionanoadsorbents

Cycle (n)	Adsorption Capacity q_n (mg/l)	Reusability Performance Rn (%)
1	82	100
2	80	97
3	78.5	95
4	77.8	94
5	77.8	94

Based on reuse experience, R_{end} was determined to be 96% (Table 1, Fig.2).

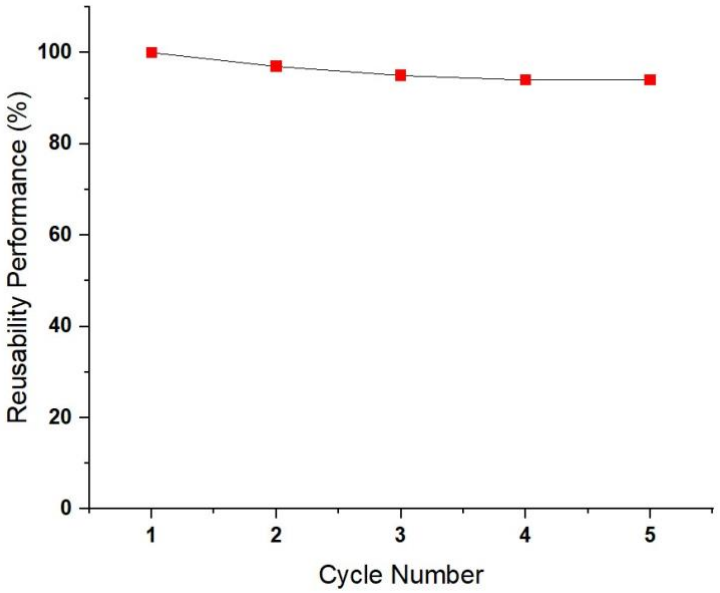

Figure 2. Reusability Performance results for PP+10%Fe_3O_4

Table 2. Desorption results of biosorbent and bionanoadsorbent

Name of the adsorbent	Ethanol (%)	Acetone (%)
PP	52.7%	65.28%
PP+10%Fe_3O_4	63.28%	71.9%

As can be seen from Table 2, the desorption process performed with acetone shows a higher desorption capacity than ethanol [26].
To calculate the economic efficiency equivalent of a biosorbent and a bio-nanoadsorbent, adsorption capacity, reuse performance, and cost are considered.

$$E_e = \frac{q_e \times R_n}{q_c}$$

E_e- Economic Efficiency
q_e- Adsorption capacity
R_n- Reusability
q_c-Adsorbent cost

As a result of the calculations, the economic efficiency for the pomegranate peel adsorbent is 2 AZN , and the economic efficiency for the PP+Fe_3O_4 bionanoadsorbent is 5.1 AZN [27].

CONCLUSION

In our research, a new type of bio-nanoadsorbent was synthesized. It was determined that the oil adsorption capacity of the synthesized bio-nanoadsorbent was 82%. The BET analysis result of the pomegranate peel/ Fe_3O_4 bio-nanoadsorbent was 67 m^2/g. BET analysis allows us to say that the synthesized bio-nanoadsorbent is an adsorbent with good absorption capacity. The desorption process during oil adsorption of the synthesized bio-nanoadsorbent was 71.9% with acetone. Based on the results obtained, it was determined that the regeneration capacity of the adsorbent was observed to be 96%. Overall, studies show that pomegranate peel/Fe3O4 bio-nanoadsorbent is based on low-waste and zero-waste technology and is a key sorption method for environmental protection.

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