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Removal of Benzyl Butyl Phthalate by Polyetheretherketone/ Polyvinylalcohol Nanocomposite Modified with Zinc Oxide Nanoparticles Adsorbent from Wastewater

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ABSTRACT

The applicability of Polyetheretherketone/polyvinylalcohol nanocomposite modified with zinc oxide nanoparticles synthesis for the removal of benzyl butyl phthalate from wastewater. Identical techniques, including BET, FT-IR, XRD, and SEM, have to characterize this unknown material. The investigation shows the applicability of adsorbent PEEK/PVA/ZnONPs, as an available, suitable, and low-cost adsorbent for adequately removing the benzyl butyl phthalate from wastewater. The impacts of variables, including benzyl butyl phthalate concentration, adsorbent, pH, and time (15 mgL^{-1}, 0.3 g, 5.0, and 60 min). Based on the received data, the adsorption of benzyl butyl phthalate on the PEEK/PVA/ZnONPs adsorbent agrees well with the Langmuir adsorption model isotherm (qm = 34.24 mgg^{-1}). The results of the thermodynamic parameter showed a negative enthalpy (-77.0 KJ/mol), a negative Gibbs free energy (-11.7 KJ/mol), and negative entropy (-274.0 J/K.mol). This led to the conclusion that the adsorption process is energetically possible, and exothermic was also spontaneous. This work indicates that the PEEK/PVA/ZnONPs, used as an ecologically adapted, adsorbent holds promise for eliminating benzyl butyl phthalate from wastewater.

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INTRODUCTION

Presently, water scarcity is a challenge in many nations, and water pollution from the paper, cloth, printing, plastics, and chemical industries is a second challenge that has to the first (Abdel Daiem et al., 2012; Moawed et al., 2015; Rafieyan et al., 2022). Organic pollutants, and colorants, have specific chemical properties that make them harmful not only to humans but also to living species in the animal and plant kingdom. Even in trace amounts, these organic pollutants should not be visible in water. They were considering that the majority of them, especially Phthalates, are carcinogenic, hazardous, and also mutagenic (Net et al., 2015; Moazzen et al., 2018; Shaida et al., 2018; Alhaddad et al., 2021). In addition, the Phthalates inhibit sunlight from entering the rivers and limit their capacity for photosynthetic processes, thus causing disequilibrium in their ecological system (Xu et al., 2007; Gao et al., 2014; Keriene and Maruska, 2022).

n- Benzyl butyl phthalate is an organic compound historically used as a plasticizer, but which has now been largely phased out due to health concerns. Benzyl butyl phthalate is one of the most frequently identified in diverse environmental samples including groundwater, river

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*Corresponding Author Email: *abrishamkarmaryam@gmail.com* water, drinking water, ocean water, soil, lake sediment and marine sediments. Benzyl butyl phthalate exerted estrogenic activities in several tests (Chatterjee and Dutta, 2008; Liu and Chen, 2010; Chen et al., 2013; Fallahrodbari, 2017; Nandi et al., 2021). Benzyl butyl phthalate can be biologically degraded (Wittassek et al., 2011; Just et al., 2012; Shaida et al., 2018; Alhaddad et al., 2021). Although these microbial systems function in the laboratory under predetermined culture conditions, the bactericidal toxicants (such as heavy metals) that may in many wastes would limit their actual effectiveness. This report studied the adsorption properties of commercially-available polyetheretherketone/polyvinylalcohol nanocomposite modified with zinc oxide nanoparticles synthesis targeting one dialkyl phthalate ester, namely n-benzyl butyl phthalate.

In recent years, it has been tried to eliminate specified organics from water samples by applying diverse potential adsorbents. Membrane fouling is a significant challenge when separating membranes in industrial applications, which reduces the permeate flow rate by different mechanisms, such as forming cake and pore blockage. In addition, it can degrade the membrane and decrease its selectivity and lifetime (Safarpour et al., 2016; Jaleh et al., 2020). Membrane fouling is enormously impressed by the physicochemical properties of membranes, such as membrane pore size, surface roughness and porosity, pore morphology, and membrane hydrophobicity (Zangeneh et al., 2019; Balkanloo et al., 2020).

Zinc oxide nanoparticles are a promising material for adsorption processes. Zinc oxide nanoparticles were successfully examined as an adsorbent material for removing pollutants from aqueous solutions. ZnO is synthesized easily, low cost, eco-friendly, and stable in environmental conditions (Jazebizadeh and Khazraei, 2017; Pournamdari, 2023). ZnO nanoparticles are efficacious toward removing materials under convenient conditions, such as organic pollutants, and dyes from aqueous solutions (Li et al., 2017; Mostafa et al., 2020). Using ZnO nanoparticles can remarkably enhance the removal of phthalates from drinking water and aqueous solutions.

Novelty, it is novel to use adsorbent PEEK/PVA/ZnONPs to remove benzyl butyl phthalate from wastewater. Hence, to fill in the gap in the literature, we chose the following study: synthesis of coupling of adsorbents modified by zinc oxide, which are involved in complex mechanisms of reactions, such as photo, electro, ultrasonic, or combination processes. Containing wastewater is not a single-component system. Moreover, the effect of other contaminants on the ion removal process by the adsorbent plays an important role. The results of the present study show how significantly and efficiently selected adsorbents modified by zinc oxide can be used for the adsorption and removal of the benzyl butyl phthalate in wastewater. In addition, in the future, further studies can be done on adsorbents to remove other contaminants and ions from wastewater.

For this paper, we are interested in eliminating benzyl butyl phthalate using adsorption on this material in its native form. The impacts of the temperature and initial benzyl butyl phthalate concentration on the adsorption capacity of the benzyl butyl phthalate were studied. The isotherms and thermodynamic parameters of the process. The desorption capacity and recycling performance of the PEEK/PVA/ZnONPs were also examined, with the latter indicating excellent recycling capacity. Finally, we applied industrial wastewater treatment to simulate better the possible application of benzyl butyl phthalate removal in an industrial process.

EXPERIMENTAL

Materials and reagents

Benzyl butyl Phthalate (99%) (Chemical formula ($C_{19}H_{20}O_4$) and molecular weight 312.365 g mol^{-1}) Phthalates, (see Fig. 1), and other ions were created by dissolving them in distilled water to produce metal ion solutions at various concentrations for adsorption investigations, including n-methyl pyrrolidine (n-MP) and polyvinyl alcohol (PVA) from Merck Company,

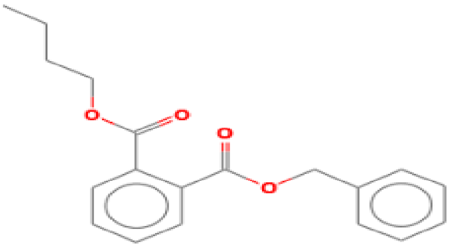

Fig. 1. The chemical structure of the benzyl butyl Phthalate.

polyetheretherketone (PEEK) from a Chinese company, ZnO nanoparticles with an average particle size of 25-30 nm from Tehran Co., Iran. Before utilization, ZnO nanoparticles at 500 °C for five hours to ensure complete drying of nanoparticles. All the above chemicals were received without any further purification.

Instrumentation

The applied instruments were as follows: The adsorption of dyes was detected using a UV-visible spectrophotometer Jenway, 6505, UK. Fourier transforms infrared (FT-IR) spectra, resulting in the investigation with Bruker-Tensor 27, Germany. The morphology of the adsorbent using SEM, JEOL Japan model # JSM6380A. The pH values of solutions were identified by the pH–meter (Hanna- Instruments 8519, pH 211, Canada) for the ultrasound-assisted adsorption procedure.

Preparation of PEEK/PVA/ZnO nanoparticle

To prepare the solution of ZnO nanoparticles (ZnONPs) at 1, 2, and 3 wt% concentrations, ZnO was dissolved in 10 mL of n-methyl pyrrolidine (n-MP) and sonicated at 45 °C for 3h. Then, SPEEK was added to ZnONP solutions separately, and the solutions were stirred under a magnet stirrer at 90 °C for 14 h. Afterward, PVA was in the mentioned solutions at 90 °C for 24 h. Finally, the Teflon-coated plate was heated at 80 °C for 24 h to evaporate the solvent and create PEEK/PVA/ZnONPs membranes. Notably, the ratio of SPEEK/PVA in the solutions and concentration of final solutions (PEEK/PVA/ZnONPs) were 70:30 (w/w), and 6.0 wt%, respectively. Moreover, to prepare a pure SPEEK/PVA membrane, SPEEK/PVA polymer at a weight ratio of 70/30 was dissolved in 10 mL of n-MP and stirred at 60 °C for 12 h. Then, the pure membrane is the same as the nano-composite membranes described earlier (Hamil et al., 2022; Pournamdari, 2023).

Sampling

In order to test the suitability of PEEK/PVA/ZnONPs adsorbent used in industrial effluents, a volume of wastewater solution was used in a series of flasks at 25 °C. Under optimal conditions, the wastewater solution was treated using PEEK/PVA/ZnONPs adsorbent. A sample of industrial effluents was taken from a location in the city Mahshahr industrial sector of Khuzestan province, and it was filtered in preparation for a subsequent experiment.

Adsorption method

The adsorption of benzyl butyl phthalate onto PEEK/PVA/ZnONPs in batch mode operation. The equilibrium time between the adsorbents and the benzyl butyl phthalate molecule was determined in a 50 mL Erlenmeyer flask. The effects of the experimental conditions investigated include contact pH, time, temperature, benzyl butyl phthalate concentration, and adsorbent dosage. The contact time range examined is 30 – 90 min, pH of 2 – 8, a temperature of 298 –

348 K, benzyl butyl phthalate concentration of 2 – 50 mgL^{-1}, and adsorbent dose of 0.03 – 1-0 g. At each experiment, the resulting mixture was filtered, and the concentration of phthalate molecule in the filtrate was determined by UV – Vis spectrometer at the predetermined maximum wavelength for benzyl butyl phthalate adsorption capacity (q_e) and efficiency (% R) and was calculated below (Fallahrodbari, 2017; Shaida et al., 2018).

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

$$q_i = \frac{V\left(C_0 - C_e\right)}{W} \times 100 \tag{2}$$

q_e (mgg^{-1}) = the quantity of benzyl butyl phthalate adsorbed per unit mass of adsorbent, C_o (mgL^{-1}) = initial benzyl butyl phthalate concentration, C_e (mgL^{-1}) = the benzyl butyl phthalate concentration at equilibrium, V (mL) = the volume of benzyl butyl phthalate solution, and W (g) = the mass of the adsorbent (Dinari and Haghighi, 2017; Rafieyan et al., 2022).

RESULTS AND DISCUSSION

Sample characterization of adsorbent

BET; analysis of PEEK/PVA/ZnONPs as an adsorbent

The BET analyses determine the physical characteristics and porosity of the adsorbents. Specific surface area, pore diameter, and total pore volume are obtained from N_2 adsorption-desorption isotherms. Fig. 2, lists the surface properties of the PEEK/PVA/ZnONPs (Zhang, 2017; Pournamdari, 2023). The adsorption capacity of PEEK/PVA, and ZnONPs depends on the porosity and chemical reactivity of functional groups at the surface. Knowledge of surface functional groups would give insight into the adsorption capability of the adsorbent. This is because when the ZnONPs into the PEEK/PVA channels, the most probable pore diameter was reduced, indicating that the ZnONPs entered the PEEK/PVA channels (Taher et al., 2017; Pournamdari, 2023).

FTIR analysis

The FT-IR, spectra of the PEEK/PVA/ZnONPs in the 400–4000 cm^{-1} wavenumber range, as demonstrated in Fig. 3a, the FT-IR spectrum of PEEK/PVA/ZnONPs presents a clear peak at 481.85 cm^{-1} related to Zn–O, and peak at 1300-1655 cm^{-1} were associated with the groups of the

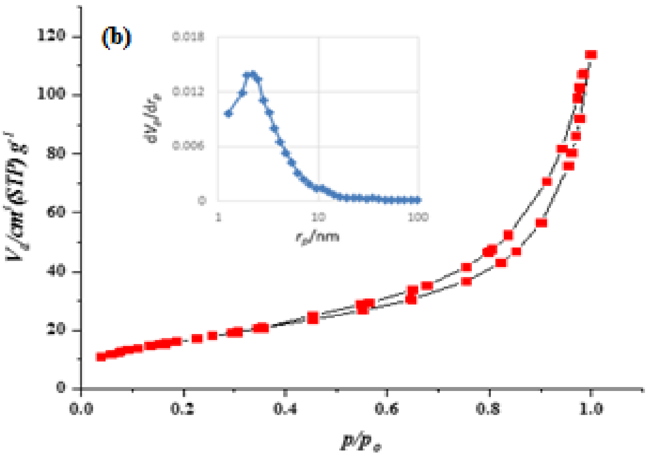

Fig. 2. N_2 adsorption–desorption isotherms of PEEK/PVA/ZnONPs.

CH-CH and (-CH$_2$)$_n$, -CH$_3$ bonds. The weak signal of the 2850 cm-1 to C=C bonds. The peak at 3485 cm^{-1} can relate to –O-H stretching (Zhang, 2017; Hamil et al., 2022; Pournamdari, 2023).

X-ray diffraction

Fig. 3b shows the XRD patterns of the PEEK/PVA membrane and the PEEK/PVA membrane modified by 2.0 ZnONPs. As seen in (Fig. 3b), in all membranes, there are specific peaks around $2\Theta = 18.4^{\circ}$ due to the existence of the crystalline surface of sulfonated polyether, ether ketone, and polyvinyl alcohol. The intensity of the diffraction peaks is related to the crystalline region of the polymer membrane by adding zinc oxide nanoparticles to the membrane. This phenomenon is caused by the influence and crystallinity of sulfonated polyether ketone and polyvinyl alcohol from the strong force resulting from the intermolecular interaction of the chains. Since, mass transfer occurs from within the amorphous regions of the membrane, the decrease in the crystalline areas and, as a result, the increase of the undeveloped parts of the polymer are favorable events for intensifying mass transfer. On the other hand, the presence of zinc oxide nanoparticles in the polymer network creates such a rigid structure that the chains do not have enough ability to move freely (Taher et al., 2017; Hamil et al., 2022). Energy-dispersive X-ray spectroscopy of the EDX spectrum after the formation of PEEK/PVA and PEEK/PVA/ZnONPs in (Fig. 3c, d) (Zhang, 2017; Hamil et al., 2022).

Morphology of prepared membranes

Filament fibers were observed for the surface of the pure membrane (Fig. 4). Moreover, SEM

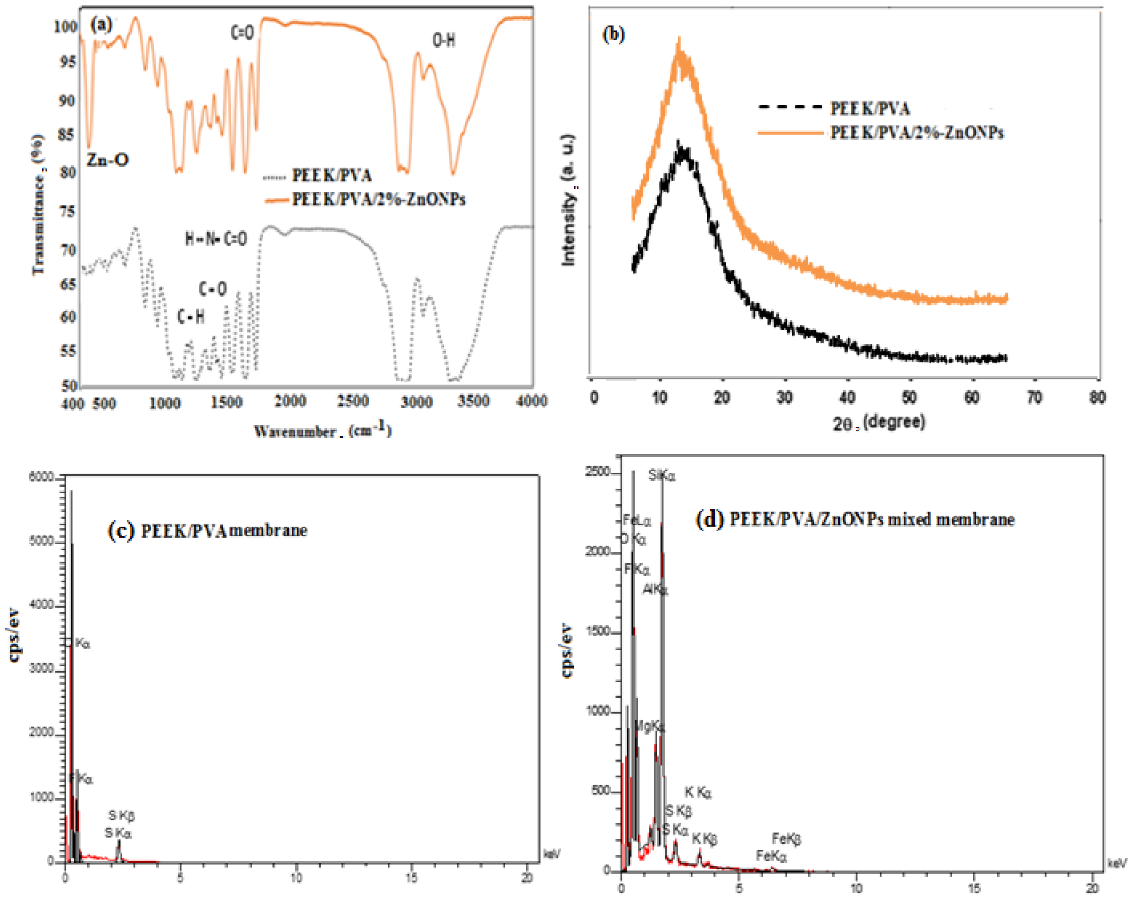

Fig. 3. (a) FT-IR spectra (b) XRD patterns (c,d) EDX spectrum of the PEEK/PVA, and PEEK/PVA/ZnONPs membrane.

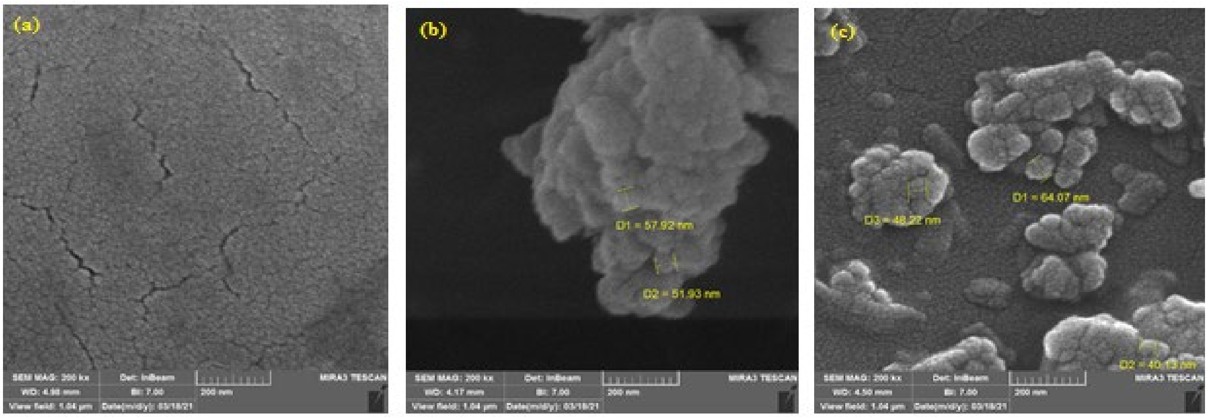

Fig. 4. (a) SEM image of PEEK/PVA (b) ZnONPs (c) PEEK/PVA PEEK/PVA/ZnONPs.

images of ZnONPs and PEEK/PVA/ZnONPs membranes (ZnONPs-modified membrane) are indicated in (Fig. 3). Accordingly, the surface structure of the PEEK/PVA/ZnONPs membrane metamorphosed into pseudo-flowering from fibrous. Furthermore, the transparent layers of the membrane surface confirm the hardening of the polymer-particle interface and an indistinct separation when the modification occurs. Notably, PEEK/PVA/ZnONPs possessed a rounded shape with a size in the range of 40–65 nm (Taher et al., 2017; Pournamdari, 2023).

Effect of pH on the adsorption

The effect of pH on the benzyl butyl phthalate removal onto PEEK/PVA/ZnONPs using the batch method. The adsorption mechanism may be a physicochemical interaction between the adsorbent/adsorbate pair (Fallahrodbari, 2017; Pournamdari, 2023). The effect of pH on the percentage of benzyl butyl phthalate removal was investigated within the range of 2 to 8. As shown in Fig. 5a, the highest percentage of benzyl butyl phthalate removal was achieved at pH 5. Considering that benzyl butyl phthalate at pH values lower than its pKa, it exists as a cationic species; at pH values equal to its pKa, as a neutral species; and at pH values higher than its pKa, as an anionic species. In alkaline conditions (pH values higher than 5), benzyl butyl phthalate becomes deprotonated, resulting in an increase in negative charge on the adsorbent surface, making it more negatively charged, and ultimately leading to electrostatic repulsion that reduces the adsorption efficiency. For pH values greater than pKa and less than 5, electrostatic attraction between the benzyl butyl phthalate and the positively charged surface of the adsorbent enhances the adsorption capacity. In this pH range, the adsorbent and benzyl butyl phthalate possess opposite surface charges, leading to increased adsorption. For pH values lower than pKa, adsorption occurs through van der Waals interactions or hydrogen bonding, and benzyl butyl phthalate remains in its molecular form, resulting in a positively charged adsorbent surface. So, the pH =5.0 is the optimum value in the benzyl butyl phthalate adsorption onto the PEEK/PVA/ZnONPs adsorbent, as shown in (Fig. 5a) (Rahmani Piani et al., 2021; Alhaddad et al., 2021; Rafieyan et al., 2022).

Effect of the dosage of absorbent

The quantity of adsorbent used during the adsorption procedure is a critical factor, considering both economic and industrial implications. It is essential to consider the potential negative effects of using too much adsorbent, as it can ultimately contribute to environmental pollution and require expensive purification processes (Rahmani Piani et al., 2022; Silori et al., 2023). It is crucial to balance the amount of adsorbent used to ensure efficient and safe adsorption processes. Fig. 5b presents the results of benzyl butyl phthalate onto PEEK/PVA/ZnONPs adsorption capacity and removal efficiency at different adsorbent doses ranging from (0.03-1.0 g). By increasing the adsorbent doses from (0.03-1.0 g), the benzyl butyl phthalate removal efficiency improved significantly, from 45% to nearly 88%. Increasing the amount of adsorbent leads to more active sites capable of removing benzyl butyl phthalate. To optimize the remaining aspects, a sorbent dosage of 0.3 g was selected for subsequent analyses, as it delivered the maximum efficiency in benzyl butyl phthalate removal (Shaida et al., 2018; Alhaddad et al., 2021; Ghazali et al., 2023).

Effect of contact time

Effect of contact time on the adsorption of benzyl butyl phthalate using PEEK/PVA/ZnONPs were defined at different contact times (30-90 min) for benzyl butyl phthalate while keeping another parameter constant. It, from Fig. 5c, that the efficiency of benzyl butyl phthalate removal increases with time until equilibrium. The maximum value of benzyl butyl phthalate removal at 60.0 min (the optimal value for the contact time parameter) for benzyl butyl phthalate, and the efficiency after it remains nearly constant due to the saturation of active sites (Fallahrodbari, 2017; Shaida et al., 2018).

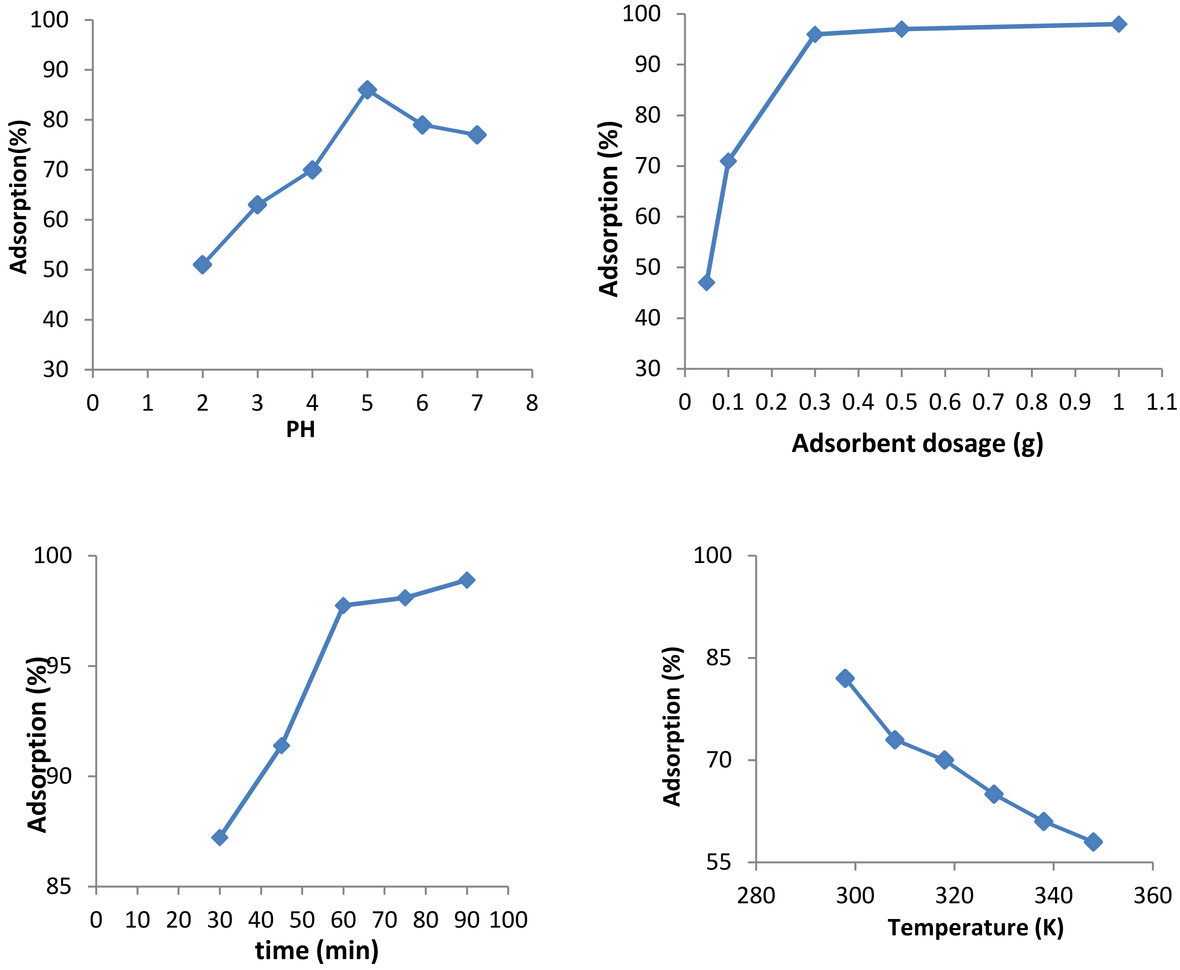

Fig. 5. (a) Effect of pH (benzyl butyl phthalate = 15 mgL^{-1}, dosage sorbent = 0.3 g, time = 60 min). (b) Effect of the dosage of absorbent (benzyl butyl phthalate = 15 mgL^{-1}, pH =5, time = 60 min). (c) Effect of contact time (benzyl butyl phthalate = 15 mgL^{-1}, pH =5, dosage sorbent = 0.3 g). (d) Effect of temperature (benzyl butyl phthalate = 15 mgL^{-1}, pH =5, dosage sorbent = 0.3 g, time = 60 min).

Effect of temperature

The effect of temperature is essential in the adsorption system, as a change in temperature can cause variation in the equilibrium constant and adsorption capacity of the adsorbent for a given solute. The relation between temperature and adsorption of benzyl butyl phthalate onto PEEK/PVA/ZnONPs adsorbent in (Fig. 6d), respectively. The data indicates that the removal of benzyl butyl phthalate decreases with rising temperature (the optimal value of temperature parameter for the adsorption of benzyl butyl phthalate onto adsorbent is 25 ^{o}C), as the temperature rise may decrease the adsorptive forces between benzyl butyl phthalate molecules and the active sites on the PEEK/PVA/ZnONPs adsorbent surface (Nandi et al., 2021; Pournamdari, 2023).

Adsorption isotherms studies

The results of adsorption investigations of benzyl butyl phthalate on the PEEK/PVA/ZnONPs adsorbent were examined in this paper by applying Langmuir, Freundlich, and Temkin isotherms. Batch adsorption isotherm tests were carried out by increasing the starting concentration from 2 to 50 mgL^{-1} at various temperatures.

The Langmuir isotherm depends on the material surface homogeneity notion, which states that all adsorption sites are identical and have the same energy (Shaida et al., 2018; Rahmani Piani et al., 2022; Silori et al., 2023).

The adsorption mechanism between the material and the materials particle must have a similar adsorption activation energy, which explains the presence of a monolayer of materials particles just on the material surface. Langmuir linear form is as follows:

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \qquad (3)$$

Where, qe (mg/g) represents the quantities of the material under equilibrium, C_e (g/L) represents the materials concentration in the sample at equilibrium, the Langmuir coefficient K_L (l/mg) to the value of the free energy of adsorption, with q_m (mg/g) represent the optimum amount of adsorption. The result, is shown in (Fig. 6a, and Table. 1).

The experimental Freundlich isotherm, which does not predict the saturation of the adsorbent by the pollutant, suggests monolayer adsorption in addition to a heterogeneous surface (Shaida et al., 2018; Rahmani Piani et al., 2021). The Freundlich model formula is given.

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \qquad (4)$$

Where, K_F (mg/g) represents the Freundlich coefficient, which determines the relative adsorption capacity of the adsorbent, and the experimental coefficient n is allied to the surface heterogeneity of the adsorbents. Factor n significantly affects the way the adsorption process functions (Dinari and Haghighi, 2017; Rafieyan et al., 2022). The result, is shown in (Fig. 6b, and Table. 1).

According to the Temkin isotherm, which is commonly used to describe the phenomenon of dangerous pollutants adhering to heterogeneous mechanisms (Rahmani Piani et al., 2021; Nandi et al., 2021), the heat of adsorption also decreases linearly in the existence of evenly distributed adsorption binding energies and interactions between materials and adsorbent.

The Temkin model expression has the following linear regression form:

$$q_e = B_T \, h \; C_e + B_T \, h \; A_T \qquad (5)$$

Knowing that T matches the absolute temperature in (Kelvin) units with R symbolizing the material coefficient (8.314J/mol.K), the value of the Temkin coefficient bT (J/mol) is linked with the heat of adsorption, while the optimum value of the binding energy is expressed as KT (l/mg). The result, is shown in (Fig. 6c, and Table. 1).

These models were applied at optimal dosages of adsorbent while other variables were kept at optimal conditions (Table. 1). Fitting the experimental data to these isotherm models and considering the higher values of correlation coefficients (R2 = 0.9935) for benzyl butyl phthalate, that the Langmuir isotherm is the best model to explain the benzyl butyl phthalate adsorption onto PEEK/PVA/ZnONPs. It also shows the equilibrium distribution of benzyl butyl phthalate between the solid and liquid phases (Rahmani Piani et al., 2021; Rafieyan et al., 2022; Ghazali et al., 2023).

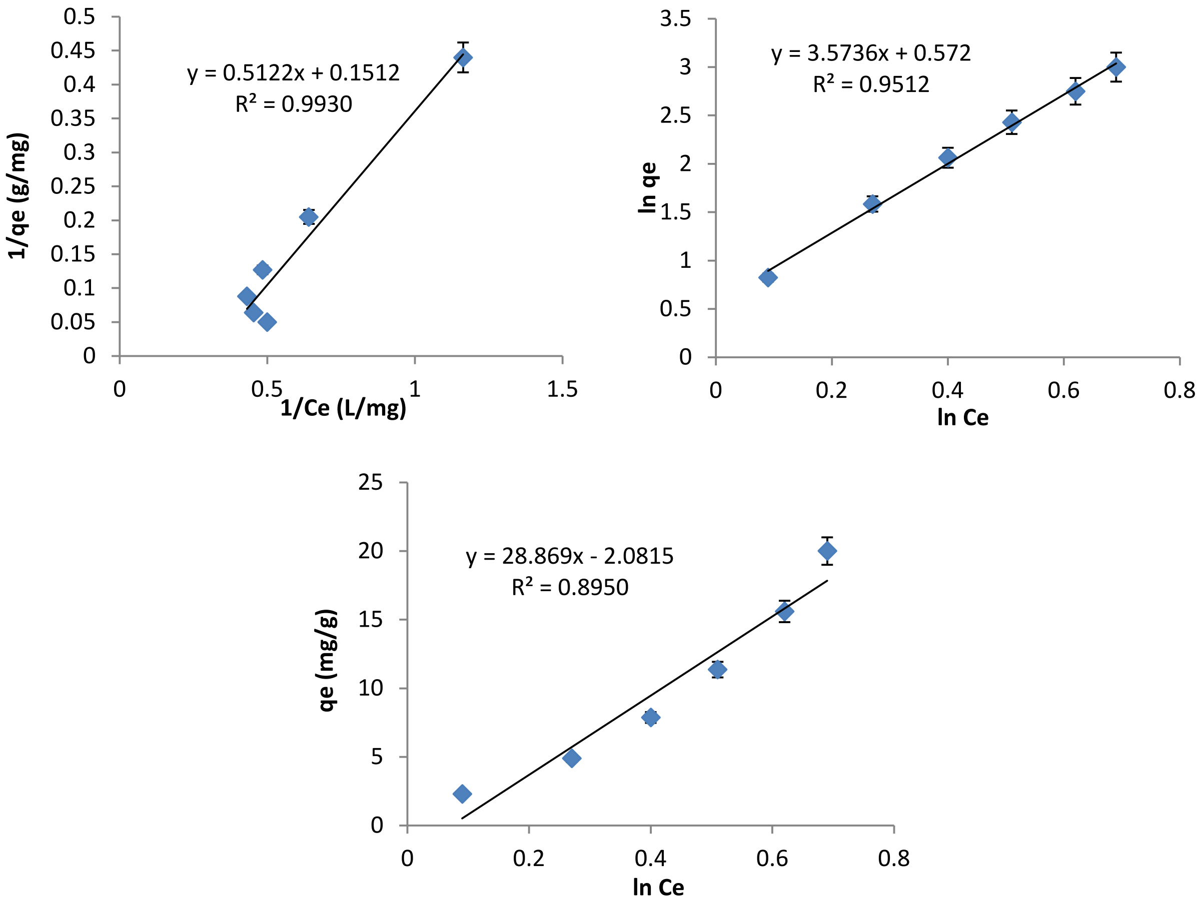

Fig. 6. Adsorption isotherm models (benzyl butyl phthalate = 15 mgL^{-1}, pH = 5, adsorbent dose = 0.3 g, time = 60 min).

Table 1. The adsorption isotherm models benzyl butyl phthalate = 15 mgL^{-1}, pH = 5, adsorbent dose = 0.3 g, time =60 min).

Isotherm	Parameters	Ad % benzyl butyl phthalate by PEEK/PVA/ZnONPs
Langmuir	q_m (mgg^{-1})	34.24
	K_L (L mg^{-1})	0.0056
	R^2	0.9930
Freundlich	n	1.006
	K_F (mg)$^{1-n}$ L^{n}g^{-1}	1.726
	R^2	0.9512
Tempkin	B_T (J mol^{-1})	12.75
	K_T (L mg^{-1})	1.2
	R^2	0.8950

Determination of thermodynamic parameters

Entropy change (ΔS°), enthalpy change (ΔH°), and change in Gibbs free energy (ΔG°) are significant thermodynamic variables for evaluating adsorption mechanism spontaneity and heat change.

$$\mathrm{LnK} = -\frac{\Delta^\circ H}{RT} + \frac{\Delta^\circ S}{R} \qquad (8)$$

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0 \qquad (9)$$

The ΔG° value of material is negative, implying the possibility, and also of spontaneity of the adsorption process; this value also means that as the temperature decreases, the adsorption process is favorable. As the temperature increases from 298 to 348 K, the adsorption performance decreases, suggesting an exothermic process (the ΔH° value is negative). This drop is related to the decreased tendency of the benzyl butyl phthalate to contact the surface of the PEEK/PVA/ZnONPs adsorbent (Shaida et al., 2018; Ghazali et al., 2023). This result is possibly justified by the degradation of the bond that links the benzyl butyl phthalate to the active sites of the material, and by the important solubility of the adsorbate when the temperature is increased. Considering the negative ΔS° results indicate that a significant benzyl butyl phthalate arrangement is established onto PEEK/PVA/ZnONPs (Fallahrodbari, 2017; Rafieyan et al., 2022).

Recycling of the Adsorbent

As seen from (Fig. 7), the benzyl butyl phthalate removal efficiency decreased slightly with

Table 2. Thermodynamic values for benzyl butyl phthalate adsorption onto PEEK/PVA/ZnONPs (benzyl butyl phthalate = 15 mg L^{-1}, pH =5, dosage sorbent = 0.3 g, time = 60 min).

Samples	T (^{O}K)	value of ΔG°(kJ/mol)	value of ΔH°(kJ/mol)	value of ΔS° (J/mol K)
benzyl butyl phthalate (15 mg/L)	298	-11.7	-77.0	-274.0
	308	-13.0		
	318	-14.3		
	328	-15.1		
	348	-15.9		

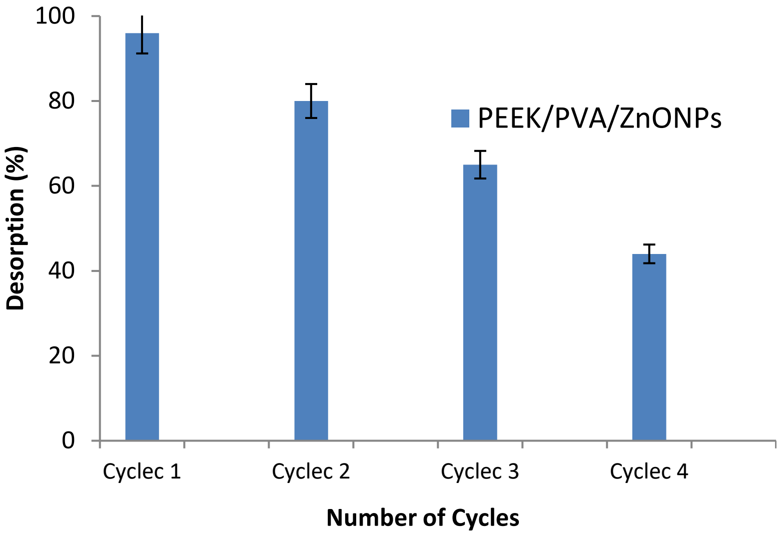

Fig. 7. Cycles adsorption of the benzyl butyl phthalate (benzyl butyl phthalate = 15 mg L^{-1}, pH =5, dosage sorbent = 0.3 g, time = 60 min).

Table 3. Results for removal of benzyl butyl phthalate from water samples.

Water samples	% Removal benzyl butyl phthalate RSD (n = 3)
Well water	99.68 ± 1.1
Tap water	95.39 ± 1.3
Wastewater	94.08 ± 1.7

Table 4. Comparison of phthalates adsorption on different adsorbents.

Phthalates	Adsorbent	Dosage sorbent	pH	Time	Adsorption capacity	References
Benzyl butyl phthalate	MTCC 4818	0.1 g	7.0	120 min	6.2 mgg^{-1}	Chatterjee and Dutta, (2008).
Benzyl butyl phthalate	Ag-MWCNTs	0.1 g	6.0	12 min	10.0 mgg^{-1}	(Fallahrodbari, 2017)
Di ethyl phthalate	Chitosan	0.5 g	5.8	240 min	42.67 mgg^{-1}	(Shaida et al., 2018)
Benzyl butyl phthalate	*Arthrobacter* sp. via micellar in a surfactant	0.1 g	7.0	120 min	10.28 mgg^{-1}	(Nandi et al., 2021)
Benzyl butyl phthalate	PEEK/PVA/ZnONPs	0.3 g	5.0	60 min	34.24 mgg^{-1}	Present study

an increase in cycle number. After four cycles, the efficiency reduced from (96.2% to 90.0 %). The result proved the stability of the PEEK/PVA/ZnONPs for the degradation of benzyl butyl phthalate in the adsorption process. In addition, the decrease in the degradation efficiency of benzyl butyl phthalate is caused by the adsorption of intermediates on the surface of PEEK/PVA/ZnONPs. Now, the necessary correction has been done, and of the section added in manuscript (Rahmani Piani et al., 2022; Pournamdari, 2023).

Application to real samples

Samples from water (50 mL) were contacted with 0.3 g of the PEEK/PVA/ZnONPs adsorbent and agitated on a rotatory shaker for 60 min. The results of the adsorption study in (Table. 3), the pollution parameters concentrations were decreased after sorption, under the predetermined optimal conditions. Subsequently, the PEEK/PVA/ZnONPs adsorbent was collected using a magnetic field, and the remaining amount of benzyl butyl phthalate was measured by UV/Vis spectrophotometer. The results of the analysis of real samples are presented in (Table. 3) (Alhaddad et al., 2021; Pournamdari et al., 2024).

Comparison with other adsorbents for removal of phthalates

Many adsorbents have to adsorb phthalates, and the achievement of wastewater treatment and their operational parameters. The adsorption capacity of PEEK/PVA/ZnONPs adsorbent was compared with previous studies, and the findings are presented in Table 6, highlighting the advantages of the current results. The table demonstrates that PEEK/PVA/ZnONPs adsorbent effectively eliminates phthalates from aqueous solution. This comparison by the maximum adsorption capacity (qmax) obtained for removal of phthalates, and individual results in (Table. 4).

CONCLUSION

Synthesized polyetheretherketone/polyvinylalcohol nanocomposite modified with zinc oxide nanoparticles, and its characterization revealed that the synthesis adsorbent has a good ability for benzyl butyl phthalate removal from wastewater. The adsorption is impacted by experimental parameters like temperature and initial benzyl butyl phthalate concentration. High temperatures do not favor the benzyl butyl phthalate adsorption mechanism, and the best elimination rate at a temperature of 298K. To investigate and optimize the influence of concentration (2-50 mg L^{-1}), process time (30-90 min), amount adsorbent (0.03-1.0 g), and pH (2-8) on the removal efficiency of benzyl butyl phthalate on the PEEK/PVA/ZnONPs adsorbent was employed. Benzyl butyl phthalate adsorption on the PEEK/PVA/ZnONPs adsorbent followed the Langmuir isotherm model, with the optimum adsorption amount achieved for PEEK/PVA/ZnONPs adsorbent being 34.24 mgg^{-1}.

Based on the Langmuir isotherm results at several temperatures, the thermodynamic parameters of adsorption are determined from these results. The negative standard enthalpy value indicates the exothermic character of the interaction of the benzyl butyl phthalate particle with the adsorbent. The adsorption mechanism is spontaneous, according to the negative results of $\Delta G°$. The adsorption mechanism shows that electrostatic interactions and the H-bonding are the main driving forces when benzyl butyl phthalate adsorbs onto PEEK/PVA/ZnONPs adsorbent. The study of the desorption and reusability mechanism of the benzyl butyl phthalate gives a positive result, after having performed four cycles of desorption-adsorption, the adsorbent keeps a critical adsorption capacity. The PEEK/PVA/ZnONPs adsorbent-based adsorbent was shown to be effective in phthalates removal from wastewater samples.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

DATA AVAILABILITY

Data will be made available on request**.**

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REFERENCES

Abdel Daiem, M.M. Rivera-Utrilla, J., Ocampo-Pérez, R., Méndez-Díaz, J.D., & Sánchez-Polo, M. (2012). Environmental impact of phthalic acid esters and their removal from water and sediments by different technologies— a review. J. Environ. Manage., 109; 164-178.

Alhaddad, F.A., Abu-Dieyeh, M., Dana Daana, D., Helaleh, M., & Al-Ghouti, M. (2021). Occurrence and removal characteristics of phthalate esters from bottled drinking water using silver modified roasted date pits. J. Environ. Health Sci. Eng., 19; 733–751.

Balkanloo, P.G., Mahmoudian, M., & Hosseinzadeh, M.T. (2020). A comparative study between MMT-Fe_3O_4/PES, MMT-HBE/PES, and MMT-acid activated/PES mixed matrix membranes. Chem. Eng. J. 396; 125188. https://doi.org/10.1016/j.cej.2020.125188.

Chatterjee, S., & Dutta, T.K. (2008). Metabolic cooperation of *Gordonia* sp. strain MTCC 4818 and *Arthrobacter* sp. strain WY in the utilization of butyl benzyl phthalate: effect of a novel coculture in the degradation of mixture of phthalates. Microbiology., 154; 3338–3346.

Chen, C.W., Chen, C.F., & Dong, C.D. (2013). Distribution of phthalate esters in sediments of Kaohsiung

Harbor. J. Taiwan Soil Sediment Contamina., 22(2); 119-131.

Dinari, M., & Haghighi, A. (2017). Surface modification of TiO_2 nanoparticle by three dimensional silane coupling agent and preparation of polyamide/modified-TiO_2 nanocomposites for removal of Cr (VI) from aqueous solutions. Prog. Org. Coatings., 110; 24–34.

Fallahrodbari, Sh. (2017). Removal of Benzyl Butyl Phthalate by adsorption onto Ag-MWCNTs: Kinetic and thermodynamic studies. Orien. J. Chem., 33(2); 910-919.

Gao, D., Li, Z., Wen, Z., & Ren, N. (2014). Occurrence and fate of phthalate esters in full-scale domestic wastewater treatment plants and their impact on receiving waters along the Songhua River in China. J. Chemosphere., 95; 24-32.

Ghazali, A.A., Marahel, F., & Mombeni Goodajdar, B. (2023). Synthesized CM-β-CD-Fe_3O_4NPs: As an Environmental Friendly and Effective Adsorbent for Elimination of Boron from Aqueous Solutions. Int. J. Environ. Anal. Chem., 103(18); 6324-6343.

Hamil, M.I., Abdulwahid, K.I., & AL-Shakban, Mu. (2022). Improvement of Corrosion and Osseointegration Characteristics for $Ti^6A_{l4}V$ Alloy by Coating with Polyetheretherketone (PEEK) and Nanohydroxyapatite Using Electrophoretic Deposition for Biomedical Applications. J. Nanostruct., 12(4); 826-841.

Jaleh, B., Zare, E., Azizian, S., Qanati, O., Nasrollahzadeh, M., & Varma, R.S. (2020). Preparation and characterization of polyvinylpyrrolidone/polysulfone ultrafiltration membrane modified by graphene oxide and titanium dioxide for enhancing hydrophilicity and antifouling properties. J. Inorg. Organomet. Polym. Mater. 30; 2213-2223.

Jazebizadeh, M.H., & Khazraei, S. (2017). Investigation of Methane and Carbon Dioxide Gases Permeability through PEBAX/PEG/ZnO Nanoparticle Mixed Matrix Membrane. Silicon., 9; 775-784.

Just, A.C., Whyatt, R.M., Perzanowski, M.S., Calafat, A.M., and Perera, F.P. (2012). Prenatal Exposure to Butylbenzyl Phthalate and Early Eczema in an Urban Cohort. Environ. Health Perspec., 120(10); 1475-1480.

Keriene, I., & Maruska, A. (2022). A review on the presence and removal of phthalates from wastewater. Urben Water J., 19(8); 769-781.

Liu, P., & Chen, C. (2010). Butyl benzyl phthalate suppresses the ATP-induced cell proliferation in human osteosarcoma HOS cells. Toxicol. Appl. Pharmacol., 244 (3); 308 -314.

Li, Z., Huang, Y., Wang, H., Wang, D., Wang, X., & Han, F. (2017). Three-dimensional hierarchical structures of ZnO nanorods as a structure adsorbent for water treatment. J. Mater. Sci. Technol., 33(8); 864-868.

Moawed, E.A., Abulkibash, A.B., & El-Shahat, M.F. (2015). Synthesis and characterization of iodo polyurethane foam and its application in removing of aniline blue and crystal violet from laundry wastewater. J. Taibah Univ. Sci., 9(1); 80-88.

Moazzen, M., Khaneghah, A.M., Shariatifar, N., Ahmadloo, M., Eş, I., Baghani, A.N., Yousefinejad, S., Alimohammadi, M., Azari, A., Dobaradaran, S., Rastkari, N., Nazmara, S., Delikhoon, M., & Jahed Khaniki, G. (2018). Multi-walled carbon nanotubes modified with iron oxide and silver nanoparticles (MWCNT-Fe_3O_4/Ag) as a novel adsorbent for determining PAEs in carbonated soft drinks using magnetic SPE-GC/MS method. Arab. J. Chem., 12(3); 1878-1892.

Mostafa, M.H., Elsawy, M.A., Darwish, M.S., Hussein, L.I., & Abdaleem, A.H. (2020). Microwave-Assisted preparation of Chitosan/ZnO nanocomposite and its application in dye removal. J. Mater. Chem. Phys., 248; 122914. doi: 10.1016/j.matchemphys.2020.122914.

Nandi, M., Tanushree Paul, T., Kumar Kanaujiya, D., Baskaran, D., Pakshirajan, K., & Pugazhenthi, G. (2021). Biodegradation of benzyl butyl phthalate and dibutyl phthalate by *Arthrobacter* sp. via micellar solubilization in a surfactant-aided system. Water Supply., 21(5); 2084–2098.

Net, S., Delmont, A., Sempere, R., Paluselli, A., & Baghdad, O. (2015). Reliable quantification of phthalates in environmental matrices (air, water, sludge, sediment and soil): A review. J. Sci. Total Environ., 515; 162-180.

Pournamdari, E. (2023). Response Surface Methodology for Adsorption of humic acid by Polyetheretherketone/ Polyvinylalcohol Nanocomposite Modified with Zinc Oxide Nanoparticles from Industrial Wastewater. Pollution., 9(3); 965-983.

Pournamdari, E., Niknam, L., Davoudi, Sh., & Khazali, F. (2024). Response Surface Methodology, and

Artificial Neural Network Model for Removal of Textile dye Reactive Yellow 105 from Wastewater using Zeolitic Imidazolate-67 Modified by Fe_3O_4 Nanoparticles. Int. J. Phytoremed., 26(1); 98-113.

Rafieyan, S.G., Ghaedi, M., Marahel, F., & Maleki. A. (2022). Application of *Terminalia catappa* wood-based activated carbon modified with CuO nanostructures coupled with H_2O_2 for the elimination of chemical oxygen demand in the gas refinery. J. Nanostruct. Chem., 12(2), 159-177.

Rahmani Piani, M., Abrishamkar, M., Mombini Godajdar, B., & Hossieni, M. (2022). Removal of Humic Acids (HAs) in Drinking Water by Adsorption onto Polysulfone/Fe_2O_3 Mixed Matrix Membrane: Study kinetics and Isotherm Analysis. J. Appl. Chem. Res., 16(1); 8-29.

Rahmani Piani, M., Abrishamkar, M., Mombini Godajdar, B., & Hossieni, M. (2021). Trihalomethanes (THMs) removal from aqueous solutions using environmental friendly and effective adsorbent onto Mespilus germanica modified by $Fe_2\,(MoO_4)_3$ nanocomposite on equilibrium, thermodynamic, and kinetics. Desal. Water Treat., 223; 288-302.

Safarpour, M., Vatanpour, V., & Khataee, A. (2016). Preparation and characterization of graphene oxide/ TiO_2 blended PES nanofiltration membrane with improved antifouling and separation performance. Desalination. 393; 65-78.

Shaida, M., Dutta, R., & Sen, A. (2018). Removal of diethyl phthalate via adsorption on mineral rich waste coal modified with chitosan. J. Mol. Liq., 261; 271-282.

Silori, R. Zang, J. Raval, N.P. Giri, Jü. Mahlknecht, B.S. Mora, A. Dueñas-Moreno, J. Tauseef, S.M., & Kumar, M. (2023). Adsorptive removal of ciprofloxacin and sulfamethoxazole from aqueous matrices using sawdust and plastic waste-derived biochar: A sustainable fight against antibiotic resistance. Bioresour Technol. 387; 129537. doi: 10.1016/j.biortech.2023.129537.

Taher, Z., Iiyas, A., Li, X., & Royl Bilad, M. (2017). Tuning the gas separation performance of fluorinated and sulfonated PEEK membranes by incorporation of zeolite 4A. J. Appl. Polym. Sci., 135(10); 45952-45964.

Wittassek, M., Koch, H.M., Angerer, J., & Brüning, T. (2011). Assessing exposure to phthalates - the human biomonitoring approach. Mol. Nutr. Food Res., 55(1); 7-31.

Xu, X.R., Li, H.B., Gu, J.D., & Li, X.Y. (2007). Kinetics of *n*-butyl benzyl phthalate degradation by a pure bacterial culture from the mangrove sediment. J. Hazard. Mater., 140; 194–199.

Zangeneh, H., Zinatizadeh, A.A., Zinadini, S., Feyzi, M., & Bahnemann, D.W. (2019). Preparation and characterization of a novel photocatalytic self-cleaning PES nanofiltration membrane by embedding a visible-driven photocatalyst boron doped-$TiO_2SiO_2/CoFe_2O_4$ nanoparticles. Separa. Purif. Technol. 209; 764-772.

Zhang, Y. (2017). Widening CO_2-facilitated transport passageways in SPEEK matrix using polymer brushes functionalized double-shelled organic sub microcapsules for efficient gas separation. J. Membr. Sci., 525; 330-341.