Response Surface Methodology for Adsorption of Humic Acid by Polyetheretherketone/ Polyvinylalcohol Nanocomposite Modified with Zinc Oxide Nanoparticles from Industrial Wastewater

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Article Info	ABSTRACT
Article type: Research Article **Article history:** Received: 16 Dec 2022 Revised: 8 Feb 2023 Accepted: 16 May 2023 **Keywords:** *humic acids (HAs)* *Adsorption* *Capacity* *Response Surface* *Methodology* *Central Composite* *Design* *Industrial Wastewater*	The applicability of Polyetheretherketone/Polyvinylalcohol Nanocomposite Modified with Zinc Oxide Nanoparticles synthesized for eliminating humic acid rapidly from industrial wastewater. Identical techniques, including BET, FTIR, XRD, and SEM have been utilized to characterize this novel material. Also, the impacts of variables including initial humic acids (HAs) concentration (X_1), pH (X_2), adsorbent dosage (X3), and sonication time (X_4) came under scrutiny using central composite design (CCD) under response surface methodology (RSM). The values of 10 mgL^{-1}, 6.0, 0.025 g, and 5.0 min were investigated through batch experiments, considered as the ideal values for humic acids (HAs) concentration, pH, adsorbent dosage, and contact time, respectively. Adsorption equilibrium and kinetic data were fitted with the Langmuir monolayer isotherm model and pseudo-second-order kinetics (R^2: 0.999) with maximum adsorption capacity (102.0 mgg^{-1}), respectively. The overall results confirmed that Polyetheretherketone/ Polyvinylalcohol Nanocomposite Modified with Zinc Oxide Nanoparticles could be a promising adsorbent material for humic acids (HAs) removal from industrial wastewater.

INTRODUCTION

Humic acid (HAs) is a kind of natural organic matter (NOMs) that is widely found in soil and surface water. Although the HAs itself is not toxic, they can play a significant role in the environmental behavior of heavy metals, pesticides, and some other pollutants (Masoudzadeh and Karachi, 2018; Chen et al., 2019). However, humic acid substances are complex high molecular weight organic compounds, with an aromatic-aliphatic character, that contain carbon, oxygen, hydrogen, nitrogen, and sulfur, and may cause water to have an undesirable taste and color and can cause blockage of membranes in membrane treatment processes, and therefore, increase the operational costs. Furthermore, humic acid can form complexes with chlorine, heavy metals, pesticides, and herbicides, creating carcinogenic compounds (Hasani et al., 2019; Derakhshani and Naghizadeh, 2018). Therefore, reducing the content of humic substances in water or changing the method of disinfection is indispensable to halt the development of

chlorinated hydrocarbons. The presence of humic substances (mainly humic acids) in almost all natural waters is often associated with a significant organic contaminations (Mamba et al., 2009; Bougdah et al., 2017). Many countries and health organizations have made strict rules to control the NOMs, concentration in drinking water, and many scholars have focused on the techniques of HA removal (Lin and Chang, 2015; Chin and Yeap, 2018). Therefore, precursors, of humic acid (HAs), and their precursors it is essential to exercise suitable methods. A variety of ways, the adsorption process as a simple and standard method is considered advantageous for the elimination of organic pollutants like humic acid (Mehrparvar et al., 2014; Lu et al., 2019).

The adsorption method is especially suitable for solving ions, environmental, gases, and metals problems and has many benefits, so it has become the focus and hot spot of research. Its popularity is due to advantages including higher efficiency, lower waste, and facile and mild operational conditions. The successfulness of adsorption techniques in the deletion of pollutants, especially those which are extremely stable in the biological degradation process via economically accomplishable soft, ways (Tao et al., 2010; Naz et al., 2016; Jin et al., 2018; Rahimi et al., 2020). Thus, the extensive utilization of adsorption techniques for the deletion of numerous chemicals from aqueous solutions seems logical (Rivas et al., 2011; Bougdah et al., 2017). In recent years, it to eliminate specified organics from water samples by applying various potential adsorbents. In this connection, magnetic nanoparticles (MNPs) as unique adsorbents thanks to their small diffusion resistance, high adsorption capacity, and large surface area have extensively been noticed (Teow et al., 2013; Eren et al., 2015; Ebrahimi et al., 2019; Mombeni Goodajdar et al., 2021).

Zinc oxide nanoparticles are promising materials in the adsorption processes. Zinc oxide nanoparticles as adsorbent material for removing pollutants from aqueous solutions. ZnO is synthesized easily, is low cost, eco-friendly, and is stable in environmental conditions (Li et al., 2017). ZnO nanoparticles are efficacious in the removal of materials under convenient conditions, such as toxic dye from aqueous solution systems (Al-Arjan, 2022). Coating chitosan with ZnO nanoparticles using assisted microwave technique shows remarkable enhancement for removing methylene blue (MB) dye from an aqueous solution (Mostafa et al., 2020). Using metal nanoparticles, special, enhancement for removing humic acids (HAs) from drinking water, and aqueous solution (Ahmad et al., 2020; Karthik Chandan et al., 2022).

Poly ether block amides are composed of two different parts of polyethylene oxide as amorphous or soft phase and polyamide interest as the crystalline or hard phase. In other words, these polymers have an amorphous part that causes the permeability of ions, gases, and metals, as well as adhesion between additives and the polymer, and the crystalline part provides the task of creating mechanical resistance in the structure of the polymer (Yousaf et al., 2014). Therefore, preparing Polyetheretherketon/Polyvinylalcohol nanocomposite modified with zinc oxide nanoparticles synthesis, especially as an effective adsorbent and alternative to exorbitant or noxious adsorbents for the elimination of humic acids (HAs) from industrial, and aqueous solution attracted our attention (Naghizadeh et al., 2016; Rahmani Piani et al., 2022).

In the present work, Polyetheretherketone/Polyvinylalcohol nanocomposite modified with zinc oxide nanoparticles as a novel adsorbent, and subsequently characterized by (IR, XRD, and SEM) analysis. Via studying the experimental conditions of pH, contact time, initial humic acids (HAs) concentration, adsorbent dosage, and the ions removal percentage. The fact that the adsorption of humic acids (HAs) follows the pseudo-second-order rate equation was clearly proven. Furthermore, that the Langmuir model could undoubtedly for the equilibrium data explanation. The pseudo-second-order model was in control of the kinetic adsorption process, which through the analysis of Kinetic models (both pseudo-first-order, and pseudo-second-order diffusion models). The capability of Polyetheretherketon/Polyvinylalcohol nanocomposite modified with zinc oxide nanoparticles in eliminating humic acids (HAs) from industrial wastewater by evidence.

EXPERIMENTAL

Chemicals and reagents

All the chemicals used are of the highest purity, and purchased from Merck (Darmstadt, Germany). humic acids (HAs) solutions were prepared synthetically by diluting a 1000 mg/L analytical grade humic acids (HAs) solution, Aluminum hydroxide (99%), n-methyl pyroledine (n-MP), and Zinc oxide (98%), Poly ether ether ketone (PEEK) from Chines Company and membrane PEEK/PVA/ZnO nanoparticle modified with Poly vinyl alcohol (PVA) was purchased from (Merck Company).

Apparatus

UV–Vis spectrophotometer model V-530 (Jasco Company, Japan). Fourier transforms infrared (FT-IR) spectra were from (FT-IR Nicolet Co, USA). Scanning electron microscopy (FESEM: MIRA III, TESCAN Company, of the Czech Republic), is used to study the morphology of samples. To set the temperature, A NBE ultra thermostat (VEB Prufgerate – Werk Medingen, Germany).

Preparation of PEEK/PVA/ZnO nanoparticle

A soluble casting method was employed to fabricate the separation membranes. Therefore, a few grams of membrane and a few ml of n-methyl pyrrolidine (n-MP) solvents were mixed and stirred for 3 hours through the instrumentality of a mechanical stirrer which ended in a uniform solution. To provide a homogeneously mixed membrane with different quantities of ZnO NPs. Initially, two solutions were synthesized, first 0.1 g of polymer was dissolved in 2 mL n-methyl pyrrolidine (n-MP) solvent and second, under constant stirring for 12 h and at 25°C, m-ZnO was separately dispersed in 2 mL n-methyl pyrrolidine (n-MP) solvent. Then, to obtain the desired weight percentages of zinc oxide nanoparticle, the solutions were mixed. The provided membrane PEEK/PVA/ZnO nanoparticles solutions were taken into glass petri dishes to get rid of the solvent, and after then dried under vacuum at 60°C for 12 h and 130°C for 3 h, membrane PEEK/PVA/ZnONPs, with Poly ether ether ketone, and Polyvinyl alcohol (PEEK/PVA) composite modified zinc oxide nanoparticle. The PEEK/PVA/ZnONPs with an equal weight ratio and after analysis, BET, XRD, FTIR, and SEM as adsorbents (Jazebizadeh and Khazraei, 2017).

Adsorption method

Generally, the sonochemical adsorption experiment was carried out in a batch mode as follows: The Erlenmeyer flask was loaded with exact quantities of humic acids (HAs) solution (50 mL) at a specified concentration of 10 mg L^{-1} and pH of 6.0 with a known amount of adsorbent (0.025 g), while the desired sonication time (5 min) was maintained at the 25°C. The adsorption trials were executed in mode, and the solution was ultrasonicated at conditions devised under RSM. At the end of the adsorption process, the sample solution was immediately centrifuged, and the analysis of the dilute phase was done to determine humic acids (HAs) concentration with the help of UV–Vis spectrophotometer at a wavelength of 380 nm (Jemeljanova et al., 2019; Ebrahimi et al., 2019). The equilibrium concentrations and removal efficiency (%) of the humic acids (HAs) were calculated according to equations (1) and (2), respectively. All experiments were conducted five times, and the final results as mean values.

$$R\% = \frac{C_{0i} - C_{ei}}{C_{0i}} \times 100 \tag{1}$$

$$q_i = \frac{V(C_{0i} - C_{ei})}{M} \times 100 \tag{2}$$

C_0 (mg/L)C0(mgL-1) in the formula refers to the initial humic acids (HAs) concentration, and C_e (mg/L)Ce(mgL-1) represents the equilibrium humic acids (HAs) concentration in an aqueous solution. V (L) shows the solution volume, and W (g) signifies the mass adsorbent (Mombeni Goodajdar et al., 2019; Rahmani Piani et al., 2022).

Central composite design (CCD)

The central composite design, for modeling, and the optimization of the effects of concentration of humic acids (HAs) (X_1), pH (X_2), amount of adsorbent (X_3), and contact time (X_4) on the ultrasonic-assisted adsorption of humic acids (HAs) by PEEK/PVA/ZnONPs. Four levels at which the R% of humic acids (HAs) as a response were determined and shown in (Tables 1, and 2). To evaluate the essential, and practical, terms for modeling the answer based on *F*-test. *P*-values less than 0.05 are generally considered a criterion for distinguishing statistically significant variables (Mombeni Goodajdar et al., 2019; Sharafi et al., 2019).

RESULTS AND DISCUSSION

Characterization of adsorbent

The evaluation special surface of PEEK/PVA/ZnONPs as an adsorbent

The Brunauer–Emmett–Teller (BET) analysis for the determination of the surface area of the PEEK/PVA/ZnONPs by N_2 adsorption before and after humic acids (HAs) adsorption (Fig. 1). The increase of surface area indicate that humic acids (HAs) are almost in almost all PEEK/PVA/ZnONPs pores after absorption. The adsorption capacity with an increase in the number of adsorbed ZnONPs, the relative partial pressure range on the adsorption isotherms gradually increases. This is because the ZnONPs, in the composite, spread into PEEK/PVA channels, making the channels narrow, and the pore volume increased. The gradual increase of BET specific surface area indicates that the ZnONPs, and has entered the PEEK/PVA pores rather than adsorbed on the outer surface of the PEEK/PVA. By comparing the pore size distribution of the samples, that with the rise in the number of adsorbed ZnONPs, the most probable pore diameter. This because when the ZnONPs, were introduced into the PEEK/PVA channels, the most probable pore diameter reduced, indicating that the ZnONPs, entered the PEEK/PVA channels, as shown in (Table. 3) (Jazebizadeh and Khazraei, 2017; Einolghozati et al., 2022).

FTIR, and XRD analysis

Fig. 2a, represents the FTIR spectra of both unmodified and modified ZnONPs. The curve refers to the FTIR spectrum of membrane PEEK/PVA fundamental, by ZnONPs, and represents that of the membrane PEEK/PVA/ZnONPs coupling components. In scrutiny, a strong signal in the range of 1005-1345 cm⁻¹ was detectable, which could result from the vibration of the hydroxyl groups on the surface of the nanoparticles (Jazebizadeh and Khazraei, 2017). Considering the b curve, it became apparent that the signals in the range 1300-1655 cm⁻¹ were associated with the group's CH–CH and (-CH₂)n,-CH₃. Therefore, that the alphabetic groups of the components related onto the surface of the nanoparticles were Zn-O. An extremely sharp band was seen at 481.85 cm⁻¹ for FT-IR spectra of the PEEK/PVA/ZnONPs, corresponding to

Table 1. Experimental factors, levels, and matrix of CCD.

Factors	levels			Star point $\alpha = 2.0$	
	Low (-1)	Central (0)	High (+1)	-α	+α
(X_1) (HAs) Concentration (mg L⁻¹)	10	15	20	5	25
(X_2) pH	5.0	6.0	7.0	4.0	8.0
(X_3) Adsorbent mass (g)	0.015	0.025	0.035	0.005	0.045
(X_4) Sonication time (min)	3.0	4.0	5.0	2.0	6.0

Table 2. The design and the response.

| Run	X_1	X_2	X_3	X_4	R% (HAs)
1	10	6	0.025	4	92.6
2	20	7	0.015	3	55.0
3	10	7	0.025	5	95.0
4	20	6	0.025	4	92.5
5	30	5	0.015	3	73.0
6	10	7	0.035	4	99.2
7	20	4	0.025	4	96.0
8	20	6	0.025	6	93.0
9	20	5	0.035	3	80.0
10	20	5	0.025	5	90.0
11	20	6	0.025	4	93.2
12	20	7	0.015	5	70.7
13	20	7	0.035	5	80.4
14	10	7	0.015	3	95.0
15	10	6	0.025	4	93.0
16	20	5	0.035	5	93.5
17	20	6	0.025	4	93.0
18	10	7	0.025	3	93.6
19	10	6	0.030	5	97.6
20	10	5	0.035	5	95.0
21	10	6	0.025	5	100.0
22	20	6	0.025	4	58.7
23	10	7	0.035	2	65.0
24	20	6	0.025	4	93.6
25	10	7	0.03	4	93.51
26	20	6	0.005	4	90.0
27	20	6	0.025	2	75.0
28	20	8	0.025	4	82.0
29	10	7	0.030	4	95.0
30	10	6	0.025	5	100.0
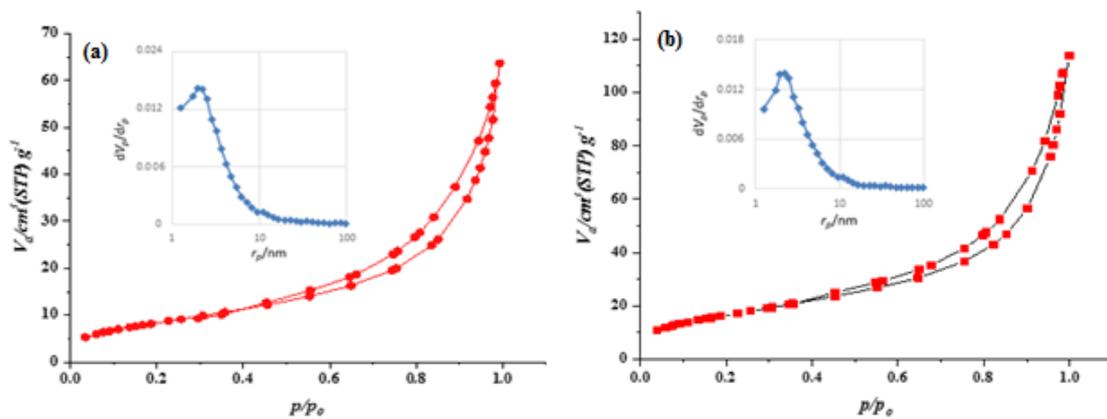
Fig. 1. Adsorption–desorption isotherms of N_2 at 77 K and Pore size distributions of for (a) PEEK/PVA.and (b) PEEK/PVA/ZnONPs.

Table 3. BET surface area and pore volume of the PEEK/PVA and PEEK/PVA/ZnONPs.

Property	Samples	
	PEEK/PVA	PEEK/PVA/ZnONPs
BET surface area (m^2/g)	31.02	60.95
Langmuir surface area (m^2/g)	31.93	63.56
t-Plot micropore area (m^2/g)	27.39	55.18
V$_{total}$ (cm^3 g^{-1})	0.09492	0.1624
Mean pore diameter (nm)	12.28	10.66
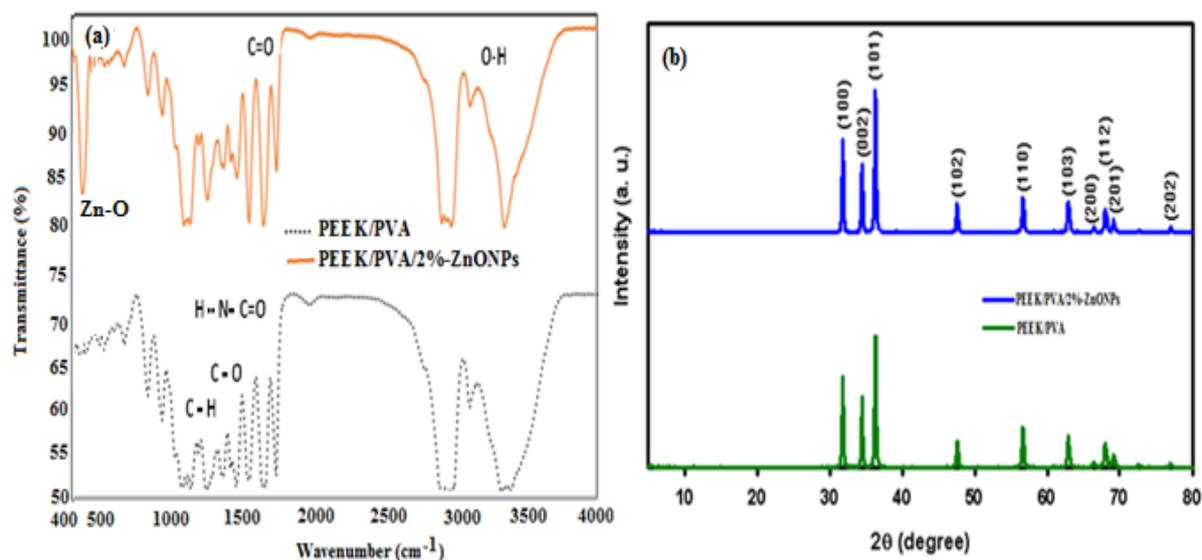
Fig. 2. (a) The IR transmittance spectrum of the prepared PEEK/PVA/ZnONPs (b) XRD of the prepared of PEEK/PVA/ZnONPs.

stretching vibrations of the Zn-O bond, suggesting a reaction between PEEK/PVA and magnetic ZnO nanoparticles. The signal of the 2850 cm^{-1} region to the b-curve of the bond C=C at the component level. Consequently, the thriving coupling of coupling groups to the surface of zinc oxide nanoparticles by the FTIR spectrum. Surface modification was successfully performed (Jazebizadeh and Khazraei, 2017; Azizi et al., 2017). In Fig. 2b, the XRD patterns of PEEK/PVA, and PEEK/PVA/ZnONPs. The there is a lack of diffraction signal in the range of 2θ angle barring one crystalline signal suggesting the presence of a small proportion of crystalline phase. Fig. 2b, ZnONPs, the clear signs at 100, 002, 101, 102, 110, 103, 200, 112, 201, and 202 prove the presence of a rutile phase which is good evidence of the crystalline form of this compound. The characteristic signals of ZnONPs and PEEK/PVA in the XRD patterns revealed that the preparation process and surface modification could not change the morphology of NPs (Jazebizadeh and Khazraei, 2017; Zhang et al., 2019).

Surface morphology

The morphological properties of PEEK/PVA/ZnONPs by SEM are exhibited in (Fig. 3), the evenness, homogeneity, orderliness, and approximate uniformity of synthesized PEEK/PVA/ZnONPs, can be observed. PEEK/PVA/ZnONPs, after surface modification, came to be uneven, bigger, and agglomerate**.** It can be seen that the particles are primarily spherical with various size distribution as they form agglomerates. Based on the particle size distribution, we obtained an average particle size in the range of 40-65 nm, very close to those determined by XRD analysis (Zhang et al., 2019; Zhang et al., 2022).
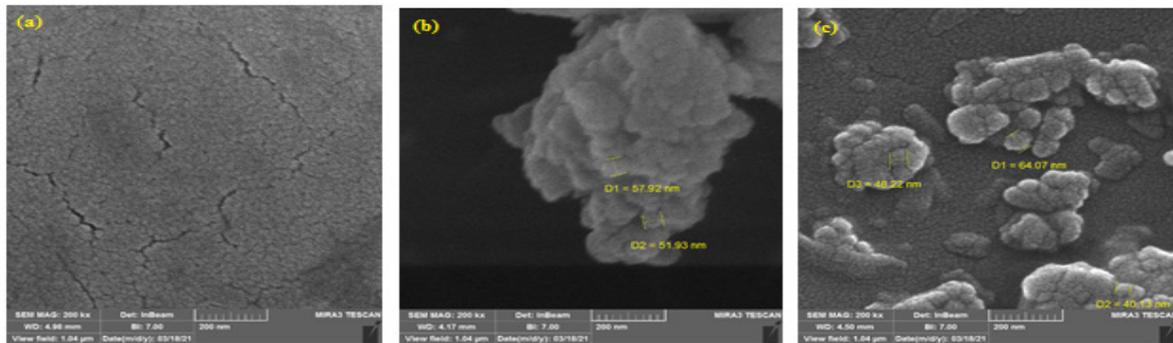
Fig. 3. SEM images of Surface (a) PEEK/PVA (b) ZnONPs (c) PEEK/PVA/ZnONPs.
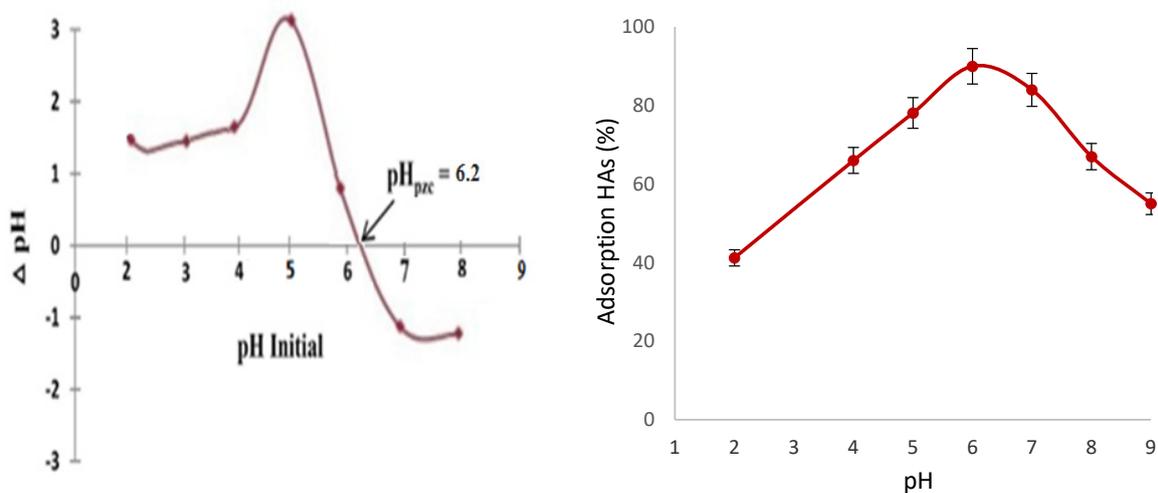

Fig. 4. pHpzc, and pH value on the adsorption of humic acids (HAs) onto PEEK/PVA/ZnONPs.

Point-of-Zero Charge (pHpzc)

The adsorption mechanism of humic acids (HAs) is better understood by the determination of the surface charge of the adsorbent which from the potential zeta study. The Point (pHpzc), variation is shown in (Fig. 4). This value indicates that the sorbent surface can acquire a positive charge at pH <pHpzc. By contrast, the surface charge of the sorbent is negative at the solution pH of 6, indicating the capability of humic acids (HAs) adsorption onto PEEK/PVA/ZnONPs. The pH value of the solution affects the surface charge of the adsorbent and the uptake behavior and efficiency of the adsorbent. As shown in (Fig. 4) (Xiong et al., 2017; Ghazalihttps://www.sciencedirect.com/author/57194516056/kiomars-sharafi et al., 2021).

Effect of pH

The pH of the adsorbent solution has as one of the most critical parameters affecting the materials removal. Therfore, pH value solution is an essential factor in humic acid (HAs) adsorption by synthesized membrane PEEK/PVA/ZnONPs. The adsorption of humic acid (HAs) on membrane PEEK/PVA/ZnONPs increases from 50 to 95% from pH range 2 to 6 and then becomes constant after a further increase in the pH value up to 9.0. The pH affects strongly affects the surface charge of membrane PEEK/PVA/ZnONPs and also the functional group dissociation of active sites. The H^+ release in the adsorption changes the pH value of the humic acid (HAs) solution by a small amount. The groups on the surface of the membrane PEEK/PVA/

ZnONPs varies with pH variation. The number of deprotonated or negatively charged groups increases with the increase in the pH of the humic acid (HAs) solution. The hydrolysis of humic acid (HAs) also increases with pH increase. Hence, the adsorption of humic acid (HAs) on membrane PEEK/PVA/ZnONPs to increase gradually with an increase in pH from 2 to 6. Most of the functional groups of membrane PEEK/PVA/ZnONPs are ionized and interacted by humic acid (HAs) with a strong electrostatic attraction, which increases the adsorption capacity of membrane PEEK/PVA/ZnONPs (Naghizadeh et al., 2016; Ebrahimihttps://www.sciencedirect.com/author/57194516056/kiomars-sharafi et al., 2019).

Modeling the process and statistical analysis

Analyzing accurate data from the RSM is another practical application of Design-Expert STATISTICA 10.0 software. RSM is a statistical method used to perform experiment analysis, modeling, and process optimization. In an RSM model, the response variable (Y) is affected by several independent variables (X_1, X_2, X_3, and X_n). RSM, the most complex model, is the second order or quadratic model, which includes the relationship between response and independent variables (contains components such as first power, interactive impacts, polynomial function, and intercept point). The quadratic model by (equation. 3) (Peeva et al., 2011; Dawoodhttps://www.sciencedirect.com/author/57194516056/kiomars-sharafi et al., 2019).

$$R\% \text{ humic acids (HAs)} = 93/084 - 10/093X_1 - 3/340X_2 + 2/4167X_3 + 4/2700X_4 - 4/9075X_1X_2$$
$$- 1/3925X_1X_3 + 3/5525X_1X_4 + 0/89500X_2X_3 - 0/17500X_2X_4 - 0/44000X_3X_4 -$$
$$3/7119X_1^2 - 1/1059X_2^2 + 0/39410X_3^2 - 2/3559X_4^2 \quad\quad (3)$$

The value of the determination coefficient for deleting humic acids (HAs) in (Table. 4), it has been noticed that the response surface quadratic model was a befitting model for predicting the function of humic acids (HAs) adsorption onto PEEK/PVA/ZnONPs (Dawoodhttps://www.sciencedirect.com/author/57194516056/kiomars-sharafi et al., 2019; Mombeni Goodajdarhttps://www.sciencedirect.com/author/57194516056/kiomars-sharafi et al., 2021).

Table 4. Analysis of Variance for the full quadratic model.

| Source of variation	Df	Sum of square	Mean square	F-value	P-value
			humic acids (HAs)		
Model	14	4353.1	310/93	751.23	< 0.0001
X_1	1	1746.2	1746.2	4218.9	< 0.0001
X_2	1	267.73	267.73	646.86	< 0.0001
X_3	1	140.17	140.17	338.65	< 0.0001
X_4	1	437.59	437.59	1057.2	< 0.0001
X_1X_2	1	385.34	385.34	930.99	< 0.0001
X_1X_3	1	31.025	31.025	74.957	< 0.0001
X_1X_4	1	201.92	201.92	487.86	< 0.0001
X_2X_3	1	12.816	12.816	30.965	< 0.0001
X_2X_4	1	0.49	0.49	1.1839	0.29375
X_3X_4	1	3.0976	3.0976	7.4839	0.015321
X_3X_5	1	225.83	225.83	545.61	< 0.0001
X_1^2	1	33.962	33.962	82.053	< 0.0001
X_2^2	1	4.3128	4.3128	10.42	0.0056318
X_3^2	1	154.12	154.12	372.37	< 0.0001
X_4^2	15	6.2085	0.4139	751.23	< 0.0001
Residual	9	5.1621	0.57357		
Lack of Fit	6	1.0464	0.1744	3.2889	0.080484
Pure Error	29	3251.3			
Cor Total					
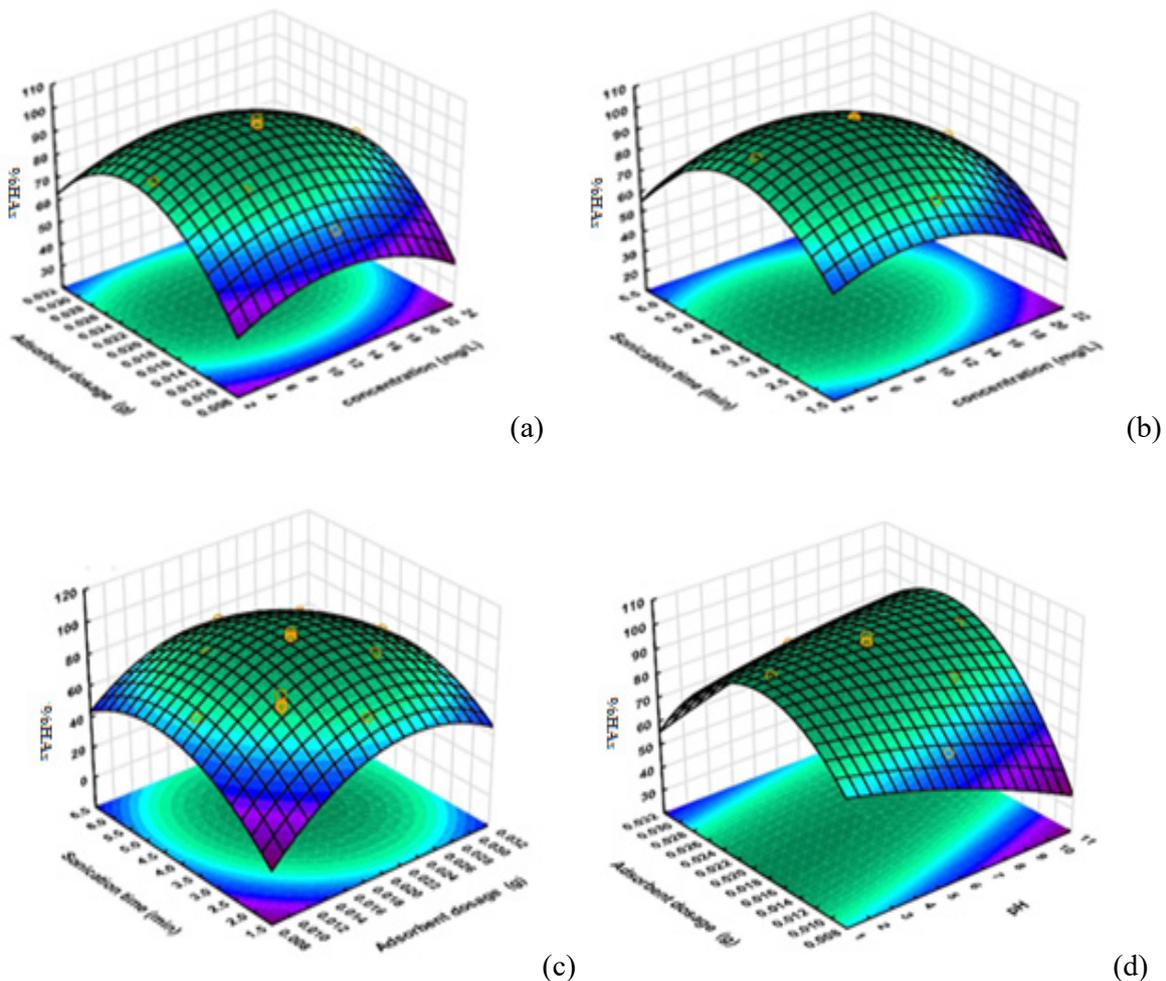
Fig. 5. Response surfaces for the humic acids (HAs) removal: (a) adsorbent dosage - initial humic acids (HAs) concentration, (b) contact time, initial humic acids (HAs) concentration. (c) contact time - adsorbent dosage, (d) humic acids (HAs) adsorbent dosage humic acids (HAs) – pH.

Response surface plots

Response surface methodology (RSM) was utilized to facilitates, the optimization and estimation of all significant interactions of variables and the relative significance of adsorption processes. Fig. 5, exhibits the three-dimensional surface response plots of this interaction. The stories for a specified pair of factual factors at optimal and fixed values of other variables (Peeva et al., 2011; Einolghozatihttps://www.sciencedirect.com/author/57194516056/kiomars-sharafi et al., 2022). A positive increase in the humic acids (HAs) removal percentage with increased adsorbent mass. A significant diminish in the removal percentage of the lower amount of PEEK/PVA/ZnONPs is attributed to the higher ratio of humic acids (HAs) molecules to the vacant sites of the adsorbent. Maximum humic acids (HAs) deletion of 100%, the optimum conditions were as follows: pH of 6.0, ultrasound time of 5.0 min, the adsorbent mass of (0.025 g), and initial humic acids (HAs) equal to 10.0 mgL^{-1}, for humic acids (HAs). Based on the excellent conformity between the experimental and prediction data, successfully for the evaluation and optimization of the influences of the adsorption - independent variables on the removal efficiency of humic acids (HAs) from aqueous media with the help of PEEK/PVA/ZnONPs (Dawoodhttps://www.sciencedirect.com/author/57194516056/kiomars-sharafi et al., 2019;
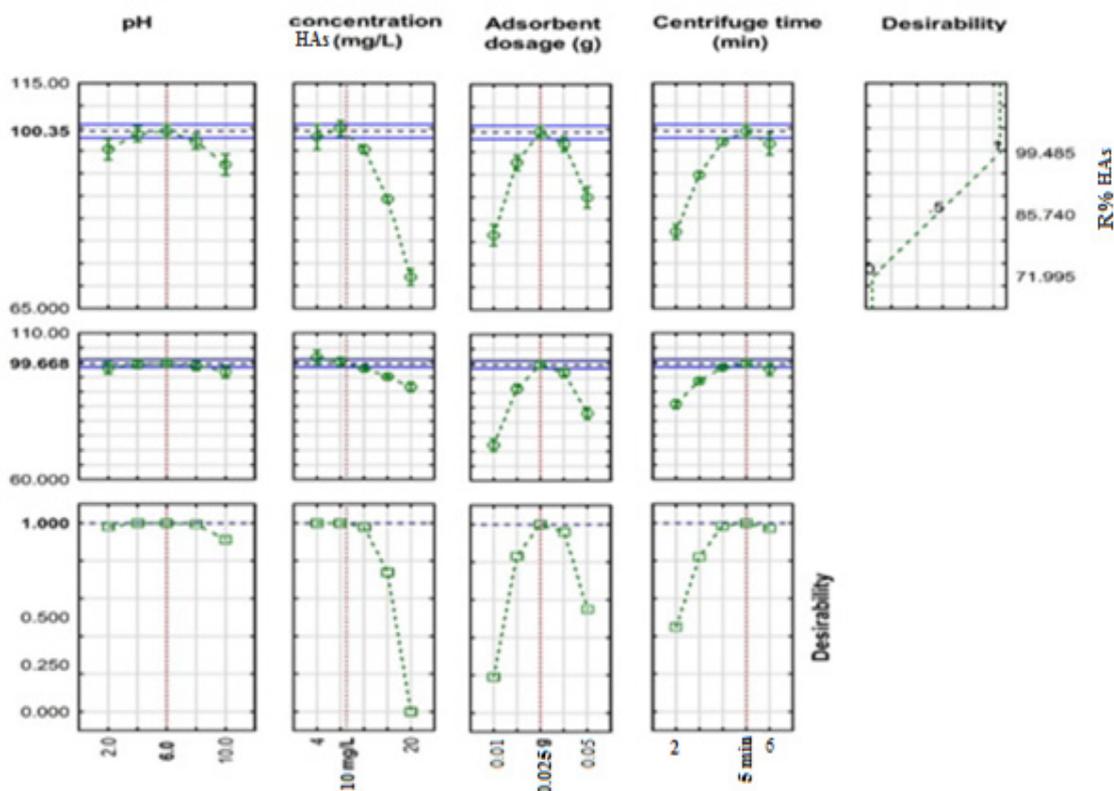
Fig. 6. Profiles for predicated values and desirability function for removal percentage of humic acids (HAs). The dashed line indicates current values after optimization.

Mombeni Goodajdarhttps://www.sciencedirect.com/author/57194516056/kiomars-sharafi et al., 2021).

Optimization of CCD

The profile for the desirable option with predicted values in the STATISTICA 10.0 software was used for the optimization of the process in (Fig. 6). Based on the excellent conformity between the experimental and prediction data, that the central composite design could be utilized successfully for the evaluation and optimization of the influences of the adsorption independent variables on the removal efficiency of humic acids (HAs) from aqueous media with the help of PEEK/PVA/ZnONPs (https://www.sciencedirect.com/author/57194516056/kiomars-sharafiSharafi et al., 2019; Einolghozatihttps://www.sciencedirect.com/author/57194516056/kiomars-sharafi et al., 2022).

Adsorption equilibrium study

The experimental adsorption equilibrium data were evaluated for studying the mechanism of humic acids (HAs) adsorption onto PEEK/PVA/ZnONPs using different models such as Langmuir, Freundlich, and Temkin isotherms (Rasuli and Mahvi, 2016; Rahmani Piani et al., 2021; https://www.sciencedirect.com/author/57194516056/kiomars-sharafiMombeni Goodajdarhttps://www.sciencedirect.com/author/57194516056/kiomars-sharafi et al., 2021). In their conventional linear form. Subsequently, their corresponding constants from the slopes and intercepts of respective lines in Table. 5. Fitting the experimental data to these isotherm models and considering the higher values of correlation coefficients ($R^2 = 0.991$) for humic acids (HAs),

Table 5. Various isotherm constants and their correlation coefficients were calculated for the adsorption of humic acids (HAs) onto PEEK/PVA/ZnONPs. [humic acids (HAs) = 10.0 mgL^{-1}, pH = 6.0, dosage sorbent = 0.025 g, time = 5.0 min, T=25^{0}C].

Isotherm	Equation	parameters	R% HAs
Langmuir	$q_e=q_m bC_e/(1+bC_e)$	q_m (mgg^{-1})	102.0
		K_L (L mg^{-1})	0.487
		R^2	0.9911
Freundlich	$\ln q_e = \ln K_F + (1/n) \ln C_e$	1/n	0.55
		K_F (mg)$^{1-n}$ Ln g^{-1}	4.09
		R^2	0.9829
Temkin	$q_e = B_1 \ln K_T + B_1 \ln C_e$	B_T (J mol^{-1})	14.15
		K_T (L mg^{-1})	6.855
		R^2	0.9634

Table 6. Kinetic parameters for the adsorption of humic acids (HAs) onto PEEK/PVA/ZnONPs. [humic acids (HAs) = 10.0 mgL^{-1}, pH = 6.0, dosage sorbent = 0.025 g, time = 5.0 min, T=25^{0}C].

Models	parameters	R% HAs
pseudo-First-order kinetic	k_1(min^{-1})	0.987
	(mgg^{-1})qe	17.92
	R^2	0.9894
pseudo-Second-order kinetic	k_2 (min^{-1})	0.154
	(mgg^{-1})qe	15.56
	R^2	0.9995
Intra particle diffusion	K_d (mg/g min$^{-1/2}$)	8.05
	C (mgg^{-1})	77.33
	R^2	0.9859
(exp) (mg/g)q_e		102.5

that the Langmuir isotherm is the best model to explain the humic acids (HAs) adsorption onto PEEK/PVA/ZnONPs, which quantitatively describes the formation of a monolayer of adsorbate on the outer surface of the PEEK/PVA/ZnONPs. It also shows the equilibrium distribution of humic acids (HAs) between the solid and liquid phases (Rasuli and Mahvi, 2016; Gomri et al., 2018; Ebrahimihttps://www.sciencedirect.com/author/57194516056/kiomars-sharafihttps://www.sciencedirect.com/author/57194516056/kiomars-sharafi et al., 2019).

The adsorption kinetics survey
    Table. 6, the values of the kinetic parameters of pseudo-first-order and second-order models as well as q$_e$,cal, q$_e$,exp. and R^2 are represented. As evident, the estimation of the correlation coefficient in the pseudo-second-order equation for the adsorption of humic acids (HAs) onto PEEK/PVA/ZnONPs was (R^2=0.9995). It is worthy of note that the estimated values of qe, cal were in excellent conformity with the experimental data. Therefore, that the pseudo second-order rate process can appropriately describe the adsorption of humic acids (HAs) onto PEEK/PVA/ZnONPs. The fitness of the film diffusion model is indicated by the close - to - unity value of R^2. However, that the straight lines did not pass through the origin indicate that resistance or the film diffusion is not probably the sole rate-limiting step (Shiyan et al., 2016; Niknam et al., 2017; Bousbahhttps://www.sciencedirect.com/author/57194516056/kiomars-sharafihttps://www.sciencedirect.com/author/57194516056/kiomars-sharafi et al., 2018). On the other hand, the inaptness of this model for the adsorption of humic acids (HAs) onto PEEK/PVA/ZnONPs adsorbents is apparent from the low values of the correlation coefficient (R^2) (Table. 6).

Table 7. The thermodynamic parameters for the adsorption of humic acids (HAs) onto PEEK/PVA/ZnONPs. [humic acids (HAs) = 10 mg L^{-1}, pH =6, dosage sorbent = 0.025 g, time = 5 min].

NOMs (mg/L)	T (^{O}K)	Kc	value of ΔG^{o} (kJ mol^{-1})	value of ΔH^{o} (kJ mol^{-1})	value of ΔS^{o} (kJ. mol^{-1} K^{-1})
humic acids (HAs) (10 mg/L)	288	-47.66	95.58	-29.24	-131.49
	308	-57.4	-103.73		
	318	-96.33	-120.85		
	328	-145.0	-135.77		
	338	-291.0	-159.40		

Adsorption thermodynamics

The standard Gibbs free energy ΔG^0 (kJ mol^{-1}), the standard enthalpy change ΔH^0 (kJ mol^{-1}), standard entropy change ΔS^0 (kJ/mol. K) using the following equations (4) and (5) (https://www.sciencedirect.com/author/57194516056/kiomars-sharafihttps://www.sciencedirect.com/author/57194516056/kiomars-sharafiHasani et al., 2018; Ebrahimi et al., 2019).

$$\Delta G^{\circ} = -RT \ln K_{ad} \qquad (4)$$

$$\ln K_{ad} = \frac{-\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \qquad (5)$$

Where, T is the temperature in Kelvin, R the gas constant (8.314 J/mol. K), ΔS° and ΔH° values can also be determined from the slope and intercept of the plot of Ln K^0 values 1/T, respectively (Table. 7). The Gibbs free energy (ΔG^0 degree of the spontaneity of the adsorption process and the low values reflect an energetically favorable adsorption process. The negative value of (ΔH°) confirms that the sorption process was exothermic, and a given amount of heat is evolved during the binding of humic acids (HAs) onto PEEK/PVA/ZnONPs on the surface of the adsorbent. The highly negative ΔS^0 values indicate a significant decrease in the degree of randomness at the solid/liquid interface during the sorption process (Naghizadehhttps://www.sciencedirect.com/author/57194516056/kiomars-sharafihttps://www.sciencedirect.com/author/57194516056/kiomars-sharafi et al., 2015; Masoudzadeh and Karachi, 2018).

*Analysis of different water samples*

To evaluate the matrix effects on the humic acids (HAs) removal, the River water samples, in Iran, were used as the real sample and spiked with various concentrations of humic acids (HAs) standard solution. The final humic acids (HAs) concentrations in water samples (Table. 8). After removal at the optimum conditions, the removal percentage was calculated (Table. 8). The results obtained from the three replicate tests on the real samples demonstrated that the synthesized sorbent can as an appropriate sorbent for humic acids (HAs) removal from the contaminated water. The selectivity experiments showed that the synthesized adsorbent had high selectivity for humic acids (HAs) removal (Adlnasab et al., 2020).

Simultaneous adsorption from a mixture of humic acids (HAs), and heavy metals

The simultaneous adsorption process for a mixture of pollutants, and heavy metals were examined in this study to test the utility of the adsorption process of membrane PEEK/PVA/ZnONPs employed as a reusable novel adsorbent for industrial casas, since most industrial wastewater contains multiple humic acids (HAs), and heavy ions. Fig. 7, shows

Table 8. Analysis of the spiked real samples with different concentrations of humic acids (HAs) (n = 3).

Samples	Added (mg L^{-1})	Founded (mg L^{-1})	RSD %	Recovery %
River water Fahlyan Fars	0.0	2.8	1.4	----
	5.0	7.7	1.6	97.6
	10.0	12.7	1.5	99.0
Hospital Namazi, Fars Waste water	0.0	3.6	1.5	----
	5.0	8.7	1.0	102.0
	10.0	13.6	1.2	102.0
River water Karaj	0.0	2.9	1.5	----
	5.0	8.0	1.8	98.0
	10.0	12.9	1.6	97.7
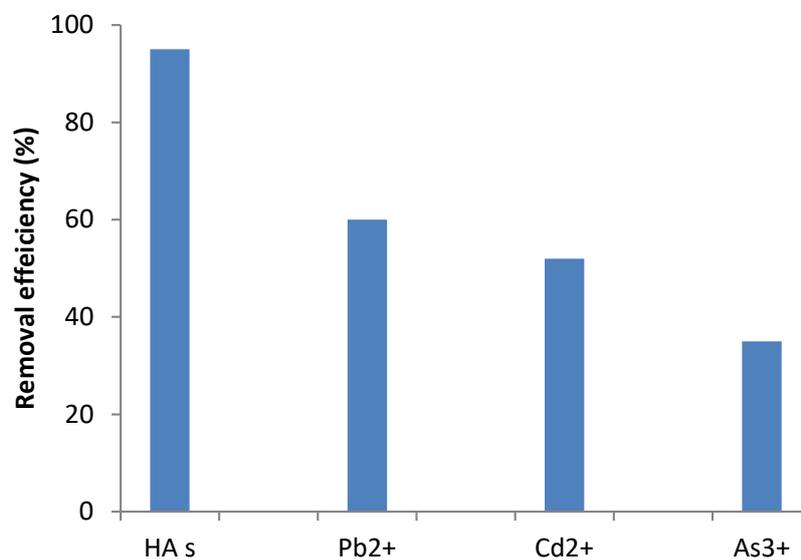
Fig. 7. Efficiency of removing a mixture of humic acids (HAs), and heavy metals using membrane PEEK/PVA/ ZnONPs, for the adsorption process. [C$_0$= 10.0 mg/L, pH = 6.0, dosage sorbent = 0.025 g, time = 5.0 min, T=25^{0}C].

the ion removal efficiency for a mixture of humic acids (HAs), and heavy metals. The data demonstrated that the elimination efficiency for humic acids (HAs) was high (95%), while the removal efficiency for Pb, Cd, and As ions were low (around 35-60%). Therefore, for the humic acids (HAs), while the minimum removal efficiency for the humic acids (HAs). This study proves that the adsorption of heavy metals by PEEK/PVA/ZnONPs employed as a reusable novel adsorbent sites, varied due to changes in the electronegativity of the heavy metals ions (Adlnasab et al., 2020).

Regeneration of adsorbent

Under optimal condition, a 10 mL of 10 mg/L humic acids (HAs) were mixed with 0.025g of PEEK/PVA/ZnONPs, and sonicated for 5.0 min. Then the mixture went under centrifugation for 5.0 min to be 99.8 %. After that, the regeneration of adsorbent was studied utilizing different solvents (ethanol, methanol, acetone, acetonitrile, N,N, dimethyl formamide, benzene, and water). For the proper regeneration of PEEK/PVA/ZnONPs, methanol showed maximum efficiency. The extraction of the humic acids (HAs) adsorbed by the adsorbent utilizing 10 mL methanol at pH 6.0 via a three-stage washing procedure. Next, for reading
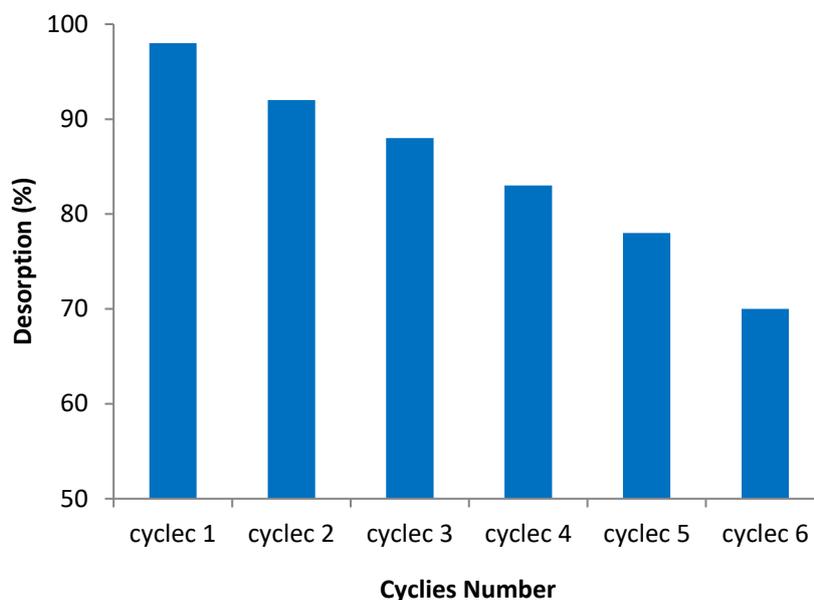
Fig. 8. Desorption of humic acids (HAs) from PEEK/PVA/ZnONPs [C_0= 10.0 mg/L, pH = 6.0, dosage sorbent = 0.025 g, time = 5.0 min, T=25^{0}C].

the adsorption of humic acids (HAs), the adjustment of the pH to 6.0 was completed. The humic acids (HAs) extraction percentages from the adsorbent were 84.2, 88.6, 93.0, 89.2 and 70.7 % for the first to fifth regeneration, respectively, which is a good indication of excellent regeneration (Naghizadehhttps://www.sciencedirect.com/author/57194516056/kiomars-sharafihttps://www.sciencedirect.com/author/57194516056/kiomars-sharafi et al., 2015; Masoudzadeh and Karachi, 2018).

Recycling of the Adsorbent

The ability to recover, and reusing of the adsorbent was tested in several steps of adsorption, and desorption. The result in (Fig. 8). As shown in Figure, 97.0 % of humic acids (HAs) from the adsorbent after the first cycle, and after 6 cycles, there were slight changes in humic acids (HAs) desorption. So, it was concluded that the desired removal of 97.0 % could be achieved after 6 cycles (https://www.sciencedirect.com/author/57194516056/kiomars-sharafihttps://www.sciencedirect.com/author/57194516056/kiomars-sharafiMombeni Goodajdar et al., 2021; Einolghozati et al., 2022).

Comparison of adsorption capacity

A comparison of the maximum adsorption capacities of different adsorbents for the removal of humic acids (HAs) in (Table. 9). The outcomes of the table clearly show that the sorption capacity of utilized sorbent in the current study is significantly high, adsorption capacity, and contact time in this article is superior to other adsorbents to remove humic acids (HAs). This variation in the adsorbed amount of the humic acids (HAs) could be attributed to various factors, such as the surface area of the adsorbent and pore volume of the adsorbent, types of functional groups that occurred onto its surface, the initial concentration of the humic acids (HAs), amount of the adsorbent used, as well as the type of the adsorption mechanism. Hence, PEEK/PVA/ ZnONPs is a promising membrane for the removal of humic acids (HAs) under the prescribed conditions as compared to other adsorbents.

Table. 9. Comparison of results for this work with other reported.

NOMs	Adsorbent	Dosage sorbent (g)	Adsorption capacity (mgg^{-1})	References
humic acids (HAs)	Aminopropyl -SBA-15	0.02	6.7 mgg^{-1}	(Tao https://www.sciencedirect.com/author/57194516056/kiomars-sharafihttps://www.sciencedirect.com/author/57194516056/kiomars-sharafiet al., 2010).
humic acids (HAs)	(ZIF-8)	1.4	14.7 mgg^{-1}	(Lin https://www.sciencedirect.com/author/57194516056/kiomars-sharafihttps://www.sciencedirect.com/author/57194516056/kiomars-sharafiet al., 2015).
humic acids (HAs)	MgONPs	0.25	5.0 mgg^{-1}	(Rasuli and Mahvi, 2016).
humic acids (HAs)	TiO$_2$NPs and ZnONPs	0.02	35.2, 37.9 and 40.2 mgg^{-1}	(https://www.sciencedirect.com/author/57194516056/kiomars-sharafihttps://www.sciencedirect.com/author/57194516056/kiomars-sharafiNaghizadeh et al., 2016).
humic acids (HAs)	Bentonite and montmorillonite nanoparticles	0.25	58.21 and 48.20 mgg^{-1}	(Derakhshani and Naghizadeh, 2018).
humic acids (HAs)	MWCNTs	1.75	12.5 mgg^{-1}	(Masoudzadeh and Karachi, 2018).
humic acids (HAs)	CM-β-CD-Fe$_3$O$_4$NPs	0.03	105.0 mgg^{-1}	(https://www.sciencedirect.com/author/57194516056/kiomars-sharafihttps://www.sciencedirect.com/author/57194516056/kiomars-sharafiMombeni Goodajdar et al., 2021).
humic acids (HAs)	PSF/Fe$_3$O$_4$ –NCs	0.1	13.333, 10.309 and 7.874 mgg^{-1}	(Rahmani Pianihttps://www.sciencedirect.com/author/57194516056/kiomars-sharafihttps://www.sciencedirect.com/author/57194516056/kiomars-sharafi et al., 2022).
humic acids (HAs)	PEEK/PVA/ZnONPs	0.025	102.0 mgg^{-1}	Present study

CONCLUSION

A thorough investigation on the effectiveness of synthesized PEEK/PVA/ZnONPs as an adsorbent for deleting humic acids (HAs) from industrial wastewater. Response surface methodology was exercised to design the experiments and quadratic model was utilized for the prediction of the variables. With the help of the central composite design (CCD) of RSM, the impacts of process variables, including humic acids (HAs) concentration, pH, adsorbent mass, and contact time on the adsorption of humic acids (HAs), came under scrutiny. Under of pH of 6.0, humic acids (HAs) concentration of 10 mg/L, adsorbent mass of 0.025 and sonication time of 5.0 min, adsorption of humic acids (HAs) onto PEEK/PVA/ZnONPs was almost 99.8%. The experimental removal efficiency of PEEK/PVA/ZnONPs got to (R^2= 0.9995) for humic acids (HAs) at optimal adsorption conditions. The excellent contribution of PEEK/PVA/ZnONPs in deleting humic acids (HAs) was confirmed when in no time. Equilibrium adsorption revealed that the system followed the Langmuir model. The highest adsorption capacity value of humic acids (HAs) with PEEK/PVA/ZnONPs to be 102.0 mgg^{-1}. The kinetics studies revealed that humic acids (HAs) deletion followed a pseudo second-order rate equation. Furthermore, desorption studies corroborated the possibility of recycling the adsorbent. Additionally, desorption studies indicated the excellent chance of reusing the adsorbent. The statistical outcomes guaranteed that the recommended equations could favorably for the adsorption of humic acids (HAs) from industrial wastewater. According to the results, PEEK/PVA/ZnONPs could, as a reusable adsorbent, it, would be an economically viable option that can lead to aqueous solutions advancement and high-quality treated effluent.

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CONFLICT OF INTEREST

The author declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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