Ultrasonic Assisted Removal of humic acids (HAs) from aqueous solutions on Uultrasonically polysulfone/ X% Fe$_2$O$_3$ mixed matrix membrane, An Experimental Design Methodology

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ABSTRACT

In the present study, the applicability of PSF/Fe$_2$O$_3$ mixed matrix membrane synthesis for eliminating humic acid rapidly from aqueous solutions. Identical techniques, including FT-IR, XRD and SEM has been utilized to characterize this novel material. The investigation showed the applicability of PSF/Fe$_2$O$_3$ mixed matrix membrane as an available, suitable and low-cost adsorbent for proper deletion of humic acid from aqueous media. Also, the impacts of variables including initial humic acids (HAs) concentration (X_1), pH (X_2), adsorbent dosage (X_3), sonication time (X_4) came under scrutiny using central composite design (CCD) under response surface methodology (RSM). Additionally, the impacts of the pH of the solution, the amount of nanoparticles, concentration of humic acids (HAs), and contact time were investigated. The experiments have been designed utilizing response surface methodology. In this current article the values of 12 mg L^{-1}, 0.03g, 7.0, 4.0 min were considered as the ideal values for humic acids (HAs) concentration, adsorbent mass, pH value and contact time respectively. The kinetics and isotherm studies proved the appropriateness of the second-order and Langmuir models for the kinetics and isotherm of the adsorption of humic acids (HAs) on the adsorbent. The adsorbent was proved to be recyclable for more than once. Since almost 99.5% of humic acids (HAs) was deleted with ideal adsorption capacities of 105 mg g^{-1} for humic acid (HAs). The overall results confirmed that PSF/Fe$_2$O$_3$ mixed matrix membrane could be a promising adsorbent material for humic acids (HAs) removal from aqueous solutions.

Keywords: Humic acids (HAs); Adsorption Capacities; polysulfone/X% Fe$_2$O$_3$ mixed matrix membranes; Response Surface Methodology (RSM); Central Composite Design (CCD).

1. INTRODUCTION

Disinfection is a process in which infective organisms or pathogenic micro-organisms are removed or deactivated. Water disinfection is performed before the distribution of it with the aim of making wastewater supplies safe and free of

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pathogen [1]. Humic acid (HA) is a kind of natural organic matters (NOMs) that are widely found in soil and surface water. Although the HA itself is not toxic, it can play a significant role in the environmental behavior of heavy metals, pesticides, and some other pollutants [2]. However, humic substances are complex high molecular weight organic compounds, with an aromatic-aliphatic character, that contain carbon, oxygen, hydrogen, nitrogen and sulfur. The relative molecular mass of humic substances ranges from a few hundred to tens of thousands. Humic acid may cause water to have an undesirable taste and color. It acts as a nutrient for the growth of bacteria in water distribution systems. Humic acid 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 [3,4]. Furthermore, HA is well-known to be a precursor of carcinogenic and mutagenic disinfection byproducts (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs) [5,6]. Therefore, reducing the content of humic substances in water or changing the method of disinfection is indispesable in order to halt the development of chlorinated hydrocarbons. The presence of humic substances (mainly humic acids) in almost all natural waters is often associated with major proportion of organic contaminations [7]. Many countries and health organizations have made strict rules to control the NOMs concentration in drinking water, and a lot of scholars have focused on the techniques of HA removal [8,9]. Therefore, for the elimination of humic acid (HAs) and their precursors it is essential to exercise suitable methods. Amongst variety of methods, the adsorption process as a

simple and standard method is considered advantageous for the elimination of organic pollutants like humic acid [10].

Polymer nanocomposites (NCs) adsorbents have been used for this purpose owing to their chemical functionality, dimension stability, adjustable surface area, easiness of handling and regeneration [12]. In the last years, there has been a strong emphasis on the development of polymeric NCs, where at least one of the dimensions of the filler material is of the order of a nanometer [13]. In the last decades, several NCs have been fabricated for the adsorptive removal of heavy metals from water and wastewater. Overall, various effects contribute determining the whole efficacy of NCs action. Composite matrix can be polysulfone (PSF). Aromatic Pas are well known as high-performance polymers because of their combination of excellent thermal, mechanical, and chemical properties that make them useful in applications for advanced technologies [14]. One of the best methods to improve membrane separation properties would be to modify existing polymers with the incorporation of fillers. Mixed matrix membranes (MMMs) combine useful molecular sieving properties of inorganic fillers with the desirable mechanical and processing properties of polymers [15]. Polymer NCs incorporate the remarkable features of both nanoparticles (NPs) and polymers: The addition of NPs to the polymer matrix has been the most usually accepted technique for manufacturing polymer NCs and the hybrids prepared with uniform dispersion of NPs can offer good mechanical strength, antifouling or self cleaning, bactericidal and also to some extent, photocatalytic properties[16]. are conventional wastewater treatment protocol based on physicochemical, chemical, and biological processes. Amongst the mentioned processes, adsorption is extensively employed for

large scale chemical, biochemical, purification and environmental recovery applications [17]. Using effective, non-toxic and low-cost adsorbents along with simple design and ease of operation made this technique beneficial and polpular. Appropriateness of the adsorbent depends on factors such as elimination capacity, treatment cost, and operating conditions [18].

Polymers like polysulfone (PSF), also has an excellent thermal and chemical resistance. These characteristic of PSF makes it a good membrane material over PPSU and PES. However, like PSF, PPSU is also hydrophobic [19] studied the heavy metal rejection property of blended PSF-based membrane, which showed maximum rejection of 98% for ions with flux [20]. However, membrane preparation from blend of PSF has not yet reported. Moreover, the blend membrane are expected to exhibit improved flux as well as antifouling property when compared to the pristine membranes. Hence, in this present study, the polymer PSF was investigated as membrane materials for the heavy metal removal and antifouling property. The polymer blends were prepared by varying PSF concentration by the phase inversion technique and studies were conducted to observe the effect of blend composition on the membrane morphology and water permeation [21]. Reported the blending of PPSU and polyetherimide (PEI) to prepare UF membrane for the humic acid (HA) separation, where the membrane exhibited good HA resistance. Therefore, polymer blends results in formation of new type of materials for UF purpose whose property can be improved by the addition of additives like polyethylene glycol (PEG), hyperbranched polyglycerol (HPG), polyvinylpyrrolidone (PVP), zinc oxide (ZnO), aluminum oxide (Al_2O_3), titanium dioxide (TiO_2) iron oxide (Fe_xO_y)

nanoparticles to PMP membrane [22]. Iron oxide nanoparticles are widely used for metal remediation due to their low toxicity and easy separation from water media [23], in addition, where the NP is composed of magnetite, a facile magnetic separation of NPs, along with associated contaminants, can be performed. However, bare magnetite nanoparticles rapidly aggregate in aqueous systems and are highly susceptible to transformations under many environmental conditions [24].

Chemical treatment and biodegradation procedures not only are based on expensive and complex processes but also produce noxious by-products. On the other hand elimination of humic acids (HAs) based on biological treatment and chemical precipitation has low efficiency and is not environmental friendly [25,26]. Therefore, preparing PSF/Fe_2O_3-NC as an alternative to exorbitant or noxious adsorbents for the elimination of humic acids (HAs) from wastewater attracted our attention. The synthesis of these unique adsorbents named PSF/Fe_2O_3-NC was easily carried out and subsequently through the instrumentality of scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) analysis, they were characterized. In humic acids (HAs) elimination process, with the help of CCD (central composite design) under RSM (response surface methodology), the scrutinizing and optimizing of the ensuing experimental conditions were performed: 1-pH of the solution, 2- contact time, 3- initial humic acids (HAs) concentration, 4- adsorbent dosage and 5- the humic acids (HAs) removal percentage. This fact that the adsorption of humic acids (HAs) follows the pseudo-second-order rate equation was clearly proven. Furthermore, it was demonstrated that the Langmuir model could undoubtedly be used for the equilibrium data explanation. The pseudo-

second-order model was in control of the kinetic of adsorption process which was confirmed through the analysis of Kinetic models (both pseudo-first-order, pseudo-second-order diffusion models). The capability of PSF/Fe$_2$O$_3$-NC in eliminating of humic acids (HAs) from wastewater was demonstrated by evidences.

2. EXPERIMENTAL
2.1. Preparation of Stock Solution
Humic acids (HAs) solutions were prepared synthetically by diluting a 2000 mg/L analytical grade humic acids (HAs) solution (Supelco Inc. Bellefonte, USA), which contains equivalent concentrations into deionized water to obtain the desired humic acids (HAs) concentration. Sodium hydroxide, hydrochloric acid, Iron Oxide. They were supplied from Merck (Darmstadt, Germany). All used chemicals were of reagent grade and utilized without further purification. For the pH adjustment, HCl (hydrochloric acid) and NaOH (sodium hydroxide) were applied [27].

2.2. Reagents and instruments
UV−vis spectrophotometer (jasco, Model UV−vis V-530, Japan). Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer (FT-IR spectrum BX, Germany). The morphology of samples was studied by scanning electron microscopy (SEM: KYKY-EM 3200, Hitachi Company, China) under an acceleration voltage of 26kV). The pH/Ion meter (model-728, Metrohm Company, Switzerland, Swiss) was used for the pH measurements. Laboratory glassware was kept overnight in 10% nitric acid solution.

2.3. Preparation of polysulfone/x%Fe$_2$O$_3$ mixed matrix membrane.
The synthesis of polysulfone/ X% Fe$_2$O$_3$ mixed matrix membrane nanoparticles was carried out at room temperature by the precipitation method. In this procedure, To obtain homogeneous mixed of PSF/m-Fe$_2$O$_3$ composites with different amounts of m-Fe$_2$O$_3$ NC (0, 5, 10 and 15 wt %), a two-step process was used. Atfirst, two solutions were synthesized: 0.1 g of polymer was dissolved in 2 mL DMSO and m-Fe$_2$O$_3$ was separately dispersed in 2 mL DMSO solution with stirring for 24 h at 25$^{\circ C}$. Then, the solutions were mixed to reach the preferred weight percentages of m-Fe$_2$O$_3$ from 5 to 15 wt %. The PSF/ m-Fe$_2$O$_3$ solutions were stirred for 24 h at 25$^{\circ C}$ and then it was sonicated for 2 h in ice bath with frequency 2.259×10^4 Hz and power 100 W. To remove the solvent, obtained PSF/ m-Fe$_2$O$_3$ solutions were poured into glass petri dishes and after 24 h at ambient temperature, PSF/ m-Fe$_2$O$_3$NCs were prepared. The solution was stirred well with the help of magnetic stirrer to maintain the homogeneous mixture. The prepared solution was after 30 min, these indicate the chemical reactions and also confirm the formation of polysulfone/ X% Fe$_2$O$_3$. The reactive solution was continuously stirred for 2 h. The powder was collected and dried in a hot air oven at 57$^{\circ C}$. The resulting mixture was washed for several times and dried in an oven leading to the synthesis of PSF/Fe$_2$O$_3$-NC.

2.4. Adsorption experiments
Based on the experimental conditions in the CCD, the adjustment of the pH of different solutions with different concentration of humic acids (HAs) was carried out utilizing concentrated HCl and/or NaOH. Through using an Erlenmeyer flask (50 mL), they were mixed completely with exact amounts of adsorbent. The trials were done at ambient temperature during predetermined sonication time in an ultrasonic. In the twilight of the adsorption process, the centrifugation of the sample solution was done promptly and the analysis of the

dilute phase was done for determining humic acids (HAs) concentration with the help of UV–Vis spectrophotometer at wavelength of 375 nm. The computation of the removal percentage of humic acids (HAs) during a given period and the calculation of the amount of humic acids (HAs) adsorbed after reaching the equilibrium (qe (mg g^{-1})) was done using the ensuing equations:

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

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

$C_\circ (mgL^{-1})$ in the above equation pertains to the initial humic acids (HAs) concentration and $C_e (mgL^{-1})$ also signifies the equilibrium humic acids (HAs) concentration in aqueous solution. The solution volume is shown by V (L) and the adsorbent mass is demonstrated by W (g). Through the instrumentality of ultrasound assisted method, the elimination of humic acids (HAs) in an adsorption combined with PSF/Fe$_2$O$_3$-NC was scrutinized. Erlenmeyer flask was loaded with exact quantities of humic acids (HAs) solution (50 mL) at specified concentration 12 mg L^{-1}, and pH of 7.0 with a known quantity of adsorbent (0.03 g) while the desired sonication time (4min) was maintained at the 25^{oC}. The adsorption trials were executed in mode and the solution was ultrasonicated at conditions devised under RSM. After performing the centrifugation for 4 min, the adsorbent PSF/Fe$_2$O$_3$-NC were separated [28,29].

2.5. Central composite design (CCD)

Central composite design (CCD) method is applied not only to decrease the number of trials and expenses but also to analyze the impact of parameters via designing experimental runs [28,29]. In this article, design expert software (version 7.0) was utilized for the analysis of the CCD outcomes. These parameters were considered: initial humic acids (HAs) concentrations (X$_1$), pH (X$_2$), adsorbent mass (X$_3$) and contact time (X$_4$). As shown in (Table 1, and 2), the number of trials was 31 at 5 levels: (-α(-2), low (-1), center (0), high (+1) and +α (+2))). To examine the reliability and validity of the developed model, ANOVA (analysis of variance) was employed. The lack of fit, regression coefficient (R^2) and the Fisher test value (F-value) were determined. With the help of second-order polynomial response equation, the mathematical relationship between the five independent parameters was obtained constantly.

Table 1. Experimental factors, levels and matrix of CCD

Factors	levels			Star pointα = 2.0	
	Low (-1)	Central (0)	High(+1)	-α	+α
(X$_1$) humic acids (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)	0.0150	0.0225	0.0350	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% humic acids (HAs)
1	20	6	0/025	4	92/63
2	30	7	0/015	3	55
3	10	7	0/025	5	95

Table 2 continued

4	20	6	0/025	4	92/5
5	30	5	0/015	3	73
6	10	7	0/035	4	99/18
7	20	4	0/025	4	96
8	20	6	0/025	6	93
9	30	5	0/035	3	80
10	30	5	0/015	5	90
11	20	6	0/025	4	93/2
12	30	7	0/015	5	70/76
13	30	7	0/035	5	80/4
14	10	7	0/015	3	95
15	20	6	0/025	4	93
16	30	5	0/035	5	93/5
17	20	6	0/025	4	93/12
18	10	7	0/025	3	93/66
19	10	7	0/030	5	97/66
20	10	5	0/035	5	95
21	10	7	0/030	4	100
22	40	6	0/025	4	58/73
23	30	7	0/035	3	65
24	20	6	0/025	4	93/62
25	10	7	0/03	4	93/52
26	20	6	0/005	4	90
27	20	6	0/025	2	75
28	20	8	0/025	4	82
29	10	7	0/035	4	95
30	20	7	0/030	4	100

2.6. Desirability function

Desirability function or DF designs a function for each specific response that provokes the final output of the general function (D) and the highest value of this output guarantees the achievement of optimum value. The governing principle and application of desirability function for the finest prognostication of real behavior of sorption system was mentioned before [29]. In the desirability profiles, the predicted levels of variables that can create the most favorable responses are recorded.

3. RESULTS AND DISCUSSION
3.1. Characterization of adsorbent

3.1.1. FTIR analysis

FT-IR spectra for pure polysulfone/ X% Fe_2O_3 mixed matrix membrane (x = 10%) are shown in Fig. 1. The vibrational frequencies for stretching bonds in PSF membrane molecule cannot be detected by FT-IR analysis. This confirms that PSF doesn't show any definite absorption peaks in the range 500 - 4000 cm^{-1}, the vibration modes located at 3451 cm^{-1} can be assigned to the O–H broad absorption mode due to the hydroxyl group in the compound. The absorption band at 1558 cm^{-1} is due to the O–H bending vibration from the water molecules adsorbed into the surface. The absorption band at 745 and

545 cm^{-1} is due to the Fe–O bending in the molecules adsorbed into the surface. There is a furthermore subtle point that no significant difference between the FT-IR spectra of pure and polysulfone/ X% Fe$_2$O$_3$ mixed matrix membranes is observed [30].

3.1.2. XRD analysis
The XRD pattern of the PSF/x% Fe$_2$O$_3$-NC mixed matrix membrane is shown in Fig.

2. The synthesized nanopowders are found to be polycrystalline in nature. All detectable peaks at 2θ= 30.2, 36.5, 38.8, 53, 60.4 and 62.4° belong to the lattice planes of (222), (311), (422), (400), (511) and (440), confirm the cubic structure of polysulfone/x% Fe$_2$O$_3$ mixed matrix membrane respectively. [31].
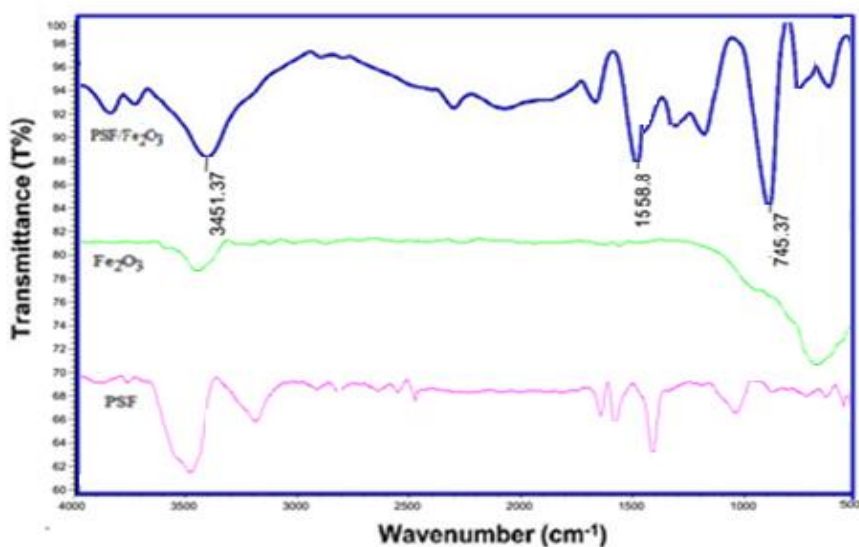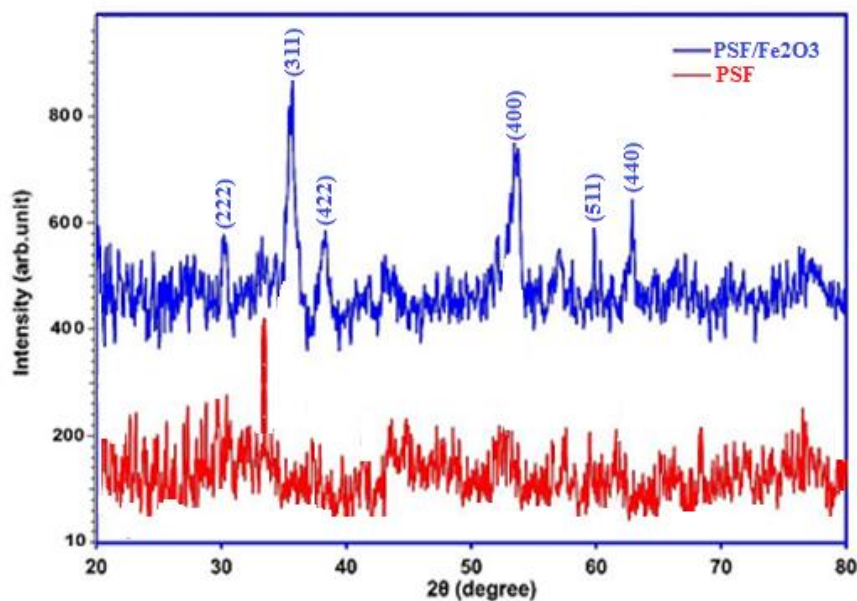

Fig. 1. FT-IR spectra of PSF/Fe2O3-NC

Fig. 2. The XRD patterns of polysulfone/ x% Fe$_2$O$_3$ mixed matrix membrane (x = 0%, 5%, 10%).

3.1.3. Morphology of prepared PSF/x% Fe₂O₃-NC mixed matrix membrane

Filamentous fibers were observed for PSF/x% Fe$_2$O$_3$-NC mixed matrix membrane surface in SEM images. Also, in Fig.3, SEM images of membrane PSF/Fe$_2$O$_3$ nanoparticles. The surface structure of the modified PSF/Fe$_2$O$_3$ membrane, based on the SEM image, metamorphosed into pseudo-flowering from fibrous. Additionally, in getting this image checked out, the apparent layers on the membrane surface confirm the hardening of the polymer-particle interface and an indistinct separation is also observed when modification was performed [32].

3.2. Modeling the process and statistical analysis

The variance analysis of all the linear, quadratic and interaction impacts of the three planning factors in relation to R% of humic acids (HAs) is represented in (Table. 3). As specified by the F-value and p-value (<0.05), the model was extremely successful in elimination of humic acids (HAs) in the polynomial equation with 95% confidence interval [33]. By considering the value of the determination coefficient for deleting humic acids (HAs), it has been noticed that the response surface quadratic model was a befitting model for predicting the function of humic acids (HAs) adsorption on PSF/Fe$_2$O$_3$-NC. The plots of experimental deletion % when juxtaposed against those computed from equations revealed a satisfactory fit. Eqs. (3), represents the codified values for the quadratic equations after ruling out the insignificant terms.

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

where Y shows the predicted response (R% of humic acids (HAs)), and the coded value of X_1 stands for the initial humic acids (HAs) concentrations, X_2 for pH, X_3 and X_4 for the adsorbent mass and ultrasound time respectively. The significance of X1, X_2, X_4, X_5, X_1X_3, X_1X_4 and all quadratic impacts for R% of humic acids (HAs) was verified [2,29].
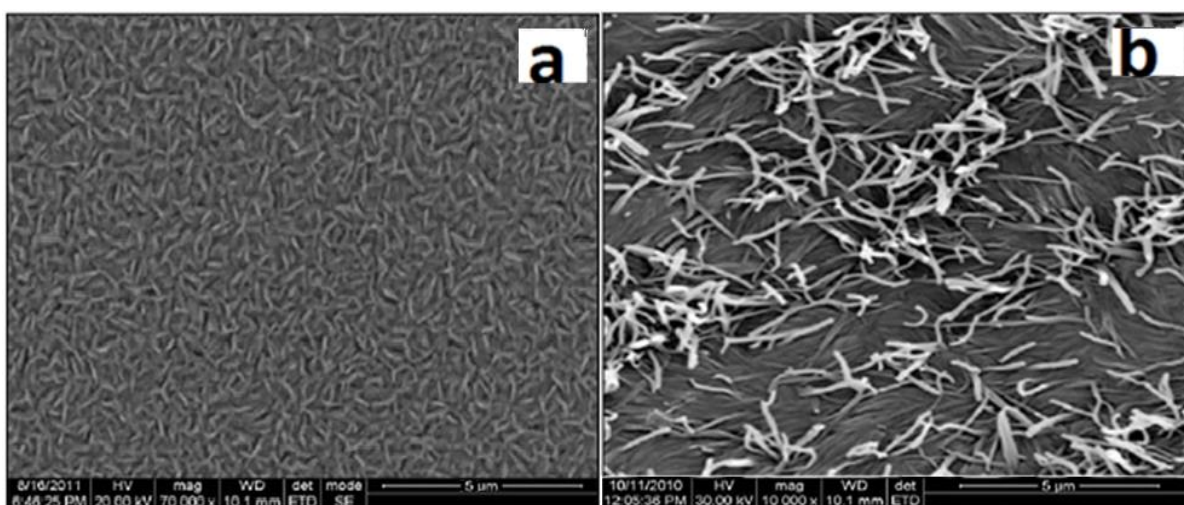

Fig. 3. The SEM images of Surface (a): membrane PSF (b): membrane PSF/m- Fe$_2$O$_3$ nanoparticles.

Table 3. Analysis of Variance for the full quadratic model

Source of variation	Df	humic acids (HAs)			
		Sum of square	Mean square	F-value	P-value
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					

3.3. Response surface plots

Response surface methodology (RSM) was utilized to ameliorate the optimization and estimation of all significance interaction of variables and the relative significance on adsorption processes. Fig. 4, exhibits the three dimensional surface response plots of this interaction. The plots were prepared for a specified pair of factual factors at optimal and fixed values of other variables [2,34]. The interaction of variables is confirmed by looking at the curves in these plots. The interaction of adsorbent mass with initial concentration of humic acids (HAs) is represented in Fig. 4a. Increase in the adsorbent dosage led to a boost in the removal percentage on the grounds of availability of more active adsorption sites, high specific surface area, and small particle size. In Fig. 4b, the relevant interaction impact of sonication time on removal percentage is demonstrated. An increase was observed in the adsorption efficiency when time was increased under

combined ultrasound/adsorbent process. In light of this figure, it is completely evident that at sonication time of 4 min, the highest humic acids (HAs) adsorption was achieved. Fig. 4d, presents the interaction of pH with initial humic acid (HAs) concentration respectively. At low initial pH, protonation of the adsorbent functional groups led to generation of positive charge and appearance of the strong attractive forces between the humic acid (HAs) molecule and adsorbent surface (increase in removal percentage). Fig. 4c, sonication time it can be concluded that maximum adsorption of humic acid (HAs) could be achieved when the sonication time was increased. The optimization of the quadratic model equations was performed after verifying the relationship between the dependent and independent variables. The use of the desirability function was to assess how well a combination of levels of process parameters meets the goals and can produce the most satisfying responses on

humic acids (HAs) adsorption within the constraints. To corroborate the optimum point for each parameter, additional experiments at the obtained optimal conditions were carried out in three replicates. Fig. 4, clearly represents the level of each process parameters, optimal response values and experimental outcomes. To achieve the maximum humic acids (HAs) deletion of 100%, the optimum conditions were as follows: pH of 7.0, ultrasound time of 4 min, adsorbent mass of (0.03g) and initial humic acids (HAs) concentration equal to 12 mgL^{-1} for

humic acids (HAs). Additionally, to examine the optimum conditions experimentally, eleven experiments under the same conditions at 25^{0}C was conducted. Based on the great conformity between the experimental and prediction data, it was confirmed 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 PSF/Fe$_2$O$_3$-NC [29].
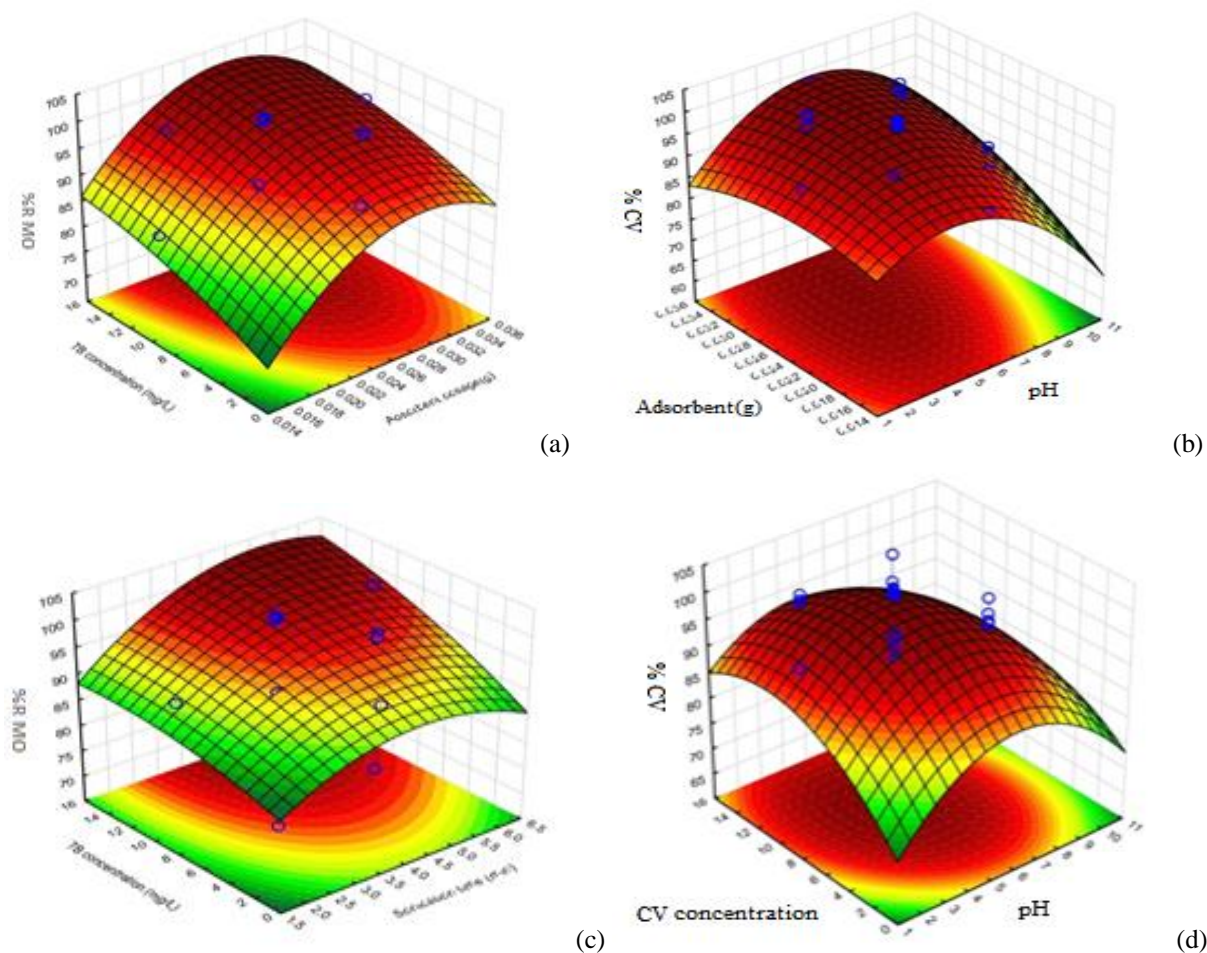

Fig. 4. Response surfaces for the humic acids (HAs) removal: (a) initial humic acids (HAs) concentration–adsorbent dosage (b) time(min)–adsorbent dosage, (c) initial humic acids (HAs) concentration– time(min) and (d) initial humic acids (HAs) concentration– pH.

3.4. Optimization of CCD by DF for Extraction Procedure

The profile for desirable option with predicted values in the STATISTICA 10.0 software was used for the optimization of the process Fig. 5. The desirability in the range of 0.0 (undesirable) to 1.0 (very desirable) was used to obtain a global function (*D*) that is the base of optimization. The CCD design matrix results were obtained as maximum (100%) for humic acids (HAs), respectively. According to these values, DF settings for either of dependent variables of removal percentages were depicted on the right hand side of Fig. 5. The results are closely co-related with the data obtained from desirability optimization analysis using CCD.

3.5. Adsorption equilibrium study

The experimental adsorption equilibrium data was evaluated for studying the mechanism of humic acids (HAs) adsorption onto PSF/Fe$_2$O$_3$-NC using different models such as Langmuir, Freundlich, Temkin, Dubinin–Radushkevich isotherms [35-39] in their conventional linear form. Subsequently, their corresponding constants were evaluated from the slopes and intercepts of
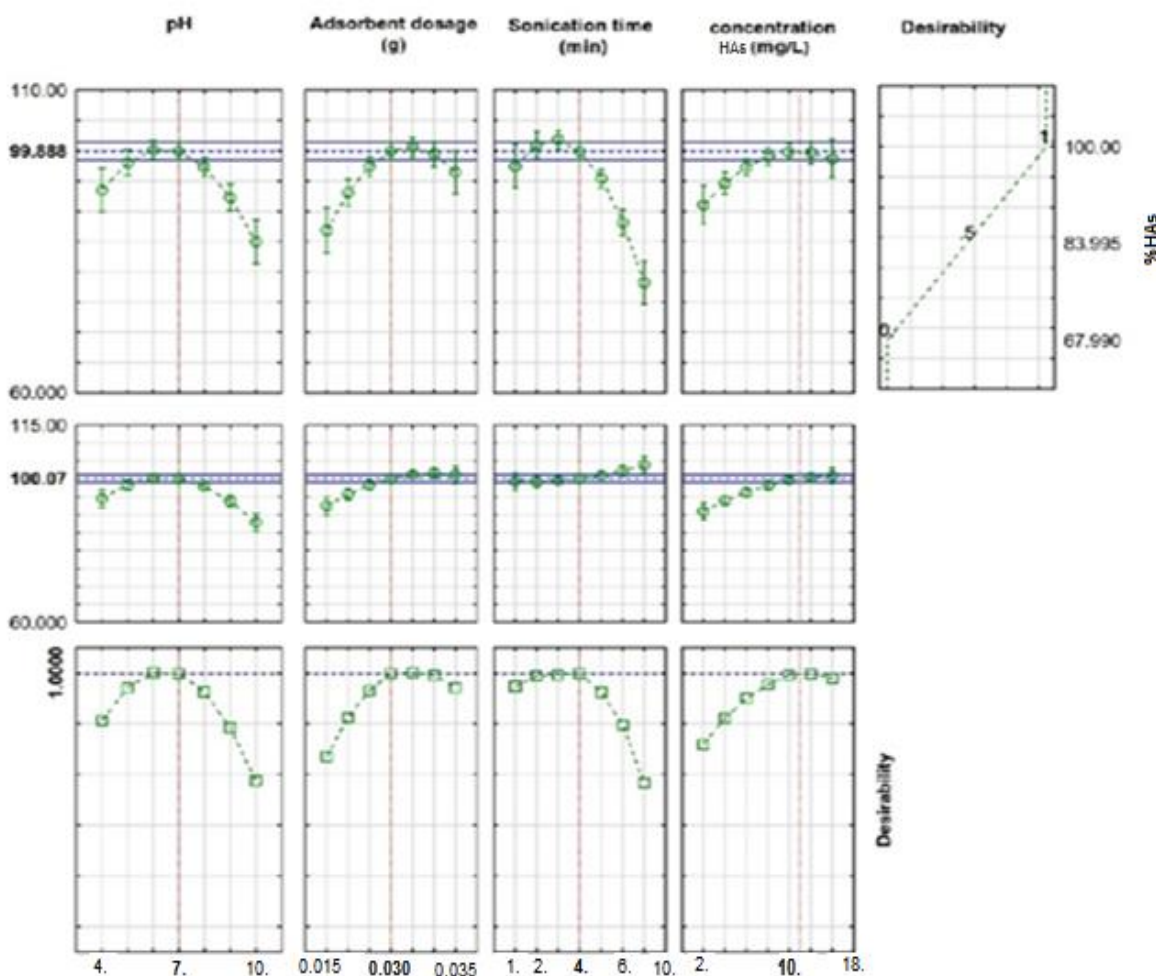

Fig. 5. Profiles for predicated values and esirability function for removal percentage of humic acids (HAs). Dashed line indicates current values after optimization.

respective lines Table.3. These models were applied at optimal dosages of adsorbent while other variables were kept at optimal condition Table. 3. Fitting the experimental data to these isotherm models and considering the higher values of correlation coefficients ($R^2 = 0.999$) for humic acids (HAs), it was concluded that the Langmuir isotherm is the best model to explain the humic acids (HAs) adsorption onto PSF/Fe_2O_3-NC, which quantitatively describes the formation of a monolayer of adsorbate on the outer surface of the PSF/Fe_2O_3-NC. It also shows the equilibrium distribution of humic acids (HAs) between the solid and liquid phase.

3.6. Kinetic study
In Table 6, the values of the kinetic parameters of pseudo-first-order and second-order models as well as qe,cal, qe,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 PSF/Fe_2O_3-NC was (R^2=0.9995). It is worthy of note that the estimated values of qe, cal were in great conformity with the experimental data. Therefore it can be

assumed that pseudo second-order rate process can appropriately describe the adsorption of humic acids (HAs) onto PSF/Fe_2O_3-NC. The fitness of film diffusion model is indicated by the close to unity value of R^2. However, taking into account the fact that the straight lines did not pass through the origin indicate that resistance or film diffusion is not probably the sole rate-limiting step. The calculation of the Elovich constants is possible from the plots of qt versus lnt [40-43]. On the other hand, the inaptness of this model for the adsorption of humic acids (HAs) onto PSF/Fe_2O_3-NC adsorbents is apparent from the low values of correlation coefficient (R^2) (Table. 5).

3.7. Comparison of humic acids (HAs) onto sorbent adsorption method with other
A comparison of the maximum adsorption capacities of different adsorbents for removal of humic acids (HAs) was also reported in Table. 6. The type and density of active sites in adsorbents which are responsible for adsorption of humic acids (HAs) from the solution result in the variation in (q_{max}) values.

Table 4. Different isotherm constants and their correlation coefficients calculated for the adsorption of humic acids (HAs) onto PSF/Fe_2O_3-NC

sotherm	Equation	parameters	Value of parameters For humic acids (HAs)
Langmuir	$q_e=q_m bC_e/(1+bC_e)$	Q_m (mg g^{-1})	105
		K_a (L mg^{-1})	0.487
		R^2	0.998
Freundlich	$\ln q_e = \ln K_F + (1/n) \ln C_e$	1/n	0.55
		K_F (L mg^{-1})	4.09
		R^2	0.982
Tempkin	$q_e = B_1 \ln K_T + B_1 \ln C_e$	B_1	14.15
		K_T (L mg^{-1})	6.855
		R^2	0.978
Dubinin-Radushkevich (DR)	$\ln q_e = \ln Q_s - B\varepsilon^2$	Q_s (mg g^{-1})	39.64
		$B \times 10^{-7}$	-1
		E (kj mol^{-1})	2237
		R^2	0.963

Table 5. Kinetic parameters for the adsorption of humic acids (HAs) onto PSF/Fe$_2$O$_3$-NC

Model	parameters	Value of parameters for humic acids (HAs)
pseudo-First-order kinetic	k_1(min-1)	0/987
	qe (calc) (mg g-1)	17/92
	R^2	0/9498
pseudo-Second-order kinetic	k_2 (min-1)	0/154
	q_e(calc) (mg g^{-1})	56/15
	R^2	0/9995
Intraparticle diffusion	K_{diff} (mg g-1 min-1/2)	8/05
	C (mg g^{-1})	33/77
	R^2	0/9859
Elovich	β (g mg-1)	0/609
	α (mg g-1 min-1)	17/74
	R^2	0/9761

Table 6. Juxtaposition of the adsorption capacities of different adsorbents for the adsorption of humic acids (HAs) onto sorbent

NOMs	Adsorbent	Dosage sorbent (g)	Adsorption capacity (mg g^{-1})	References
humic acids (HAs)	bentonite and montmorillonite nanoparticles	0.25	58.21 and 48.20 mg/g,	[4]
humic acids (HAs)	zeolitic imidazole framework-8 (ZIF-8)	1.4	14.7	[8]
humic acids (HAs)	titanium dioxide and zinc oxide nanoparticles	0.02	35.2, 37.9 and 40.2	[14]
humic acids (HAs)	aminopropyl functionalized SBA-15	0.2	6.7	[18]
humic acids (HAs)	activated carbon from raw maize tassel	0.05	3.0	[25]
humic acids (HAs)	MWCNTs modified by N-(3-nitro-benzylidene)-N-trimethoxysilylpropyl-ethane-1,2-diamine	1.75	12.5	[34]
humic acids (HAs)	MgO nanoparticles	0.1	5.0	[37]
humic acids (HAs)	Polysulfone/x% Fe$_2$O$_3$ membrane mixed matrix nano composite	0.03	105	Present study

4. CONCLUSION

A thorough investigation was performed on the effectiveness of synthesized PSF/Fe$_2$O$_3$-NC as an adsorbent for the deletion of humic acids (HAs) from aqueous solutions. Response surface methodology was exercised to design the experiments and quadratic model was utilized for the prediction of the variables. With the help of central composite design (CCD) of RSM, the impacts of process variables including humic acids (HAs) concentration, pH, adsorbent mass and contact time on adsorption of humic acids

(HAs) came under scrutiny. Under the conditions of pH of 7.0, humic acids (HAs) concentration 12 mg L^{-1}, adsorbent mass of 0.03 and sonication time of 4.0 min, the adsorption of humic acids (HAs) onto PSF/Fe_2O_3-NC was almost 99.8%. The experimental removal efficiency of PSF/Fe_2O_3-NC got to (R^2= 0.9995) for humic acids (HAs) at optimal adsorption conditions. The excellent contribution of PSF/Fe_2O_3-NC in deleting humic acids (HAs) was confirmed when the lowest errors were obtained in no time. Equilibrium adsorption revealed that the system followed the Langmuir model. The highest adsorption capacity value of humic acids (HAs) with PSF/Fe_2O_3-NC was observed to be 105 mgg^{-1}. The kinetics studies brought to light that humic acids (HAs) deletion followed pseudo second-order rate equation. Furthermore, desorption studies corroborated the possibility of recycling the adsorbent. With reference to the results of the linear regression-based analysis, it was reported that a satisfactory adsorbing performance onto PSF/Fe_2O_3-NC was predictable from the empirical models with significant determination coefficients of R^2= 0.9998. Additionally, the statistical outcomes guaranteed that the recommended equations could favourably be employed for the adsorption of humic acids (HAs) from aqueous solutions. Further investigations on the suitability of this adsorbent for the deletion of other materials have been suggested. Also it was suggested to investigate on the suitability of this adsorbent in industrial application. The findings proved the appropriateness of the present precedure for the successful deletion of Pollutants from aqueous solution.

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REFERENCES
[1] X. Chen, Y. Xu, M. Fan, Y. Chen, S. Shen, J. Environ. Manage. 235 (2019) 350.

[2] E. Pournamdari, Pollution. 9(3) (2023) 1-18.

[3] G. Hasani, A. Maleki, H. Daraei, R. Ghanbari, M. Safari, G. McKay, K. Yetilmezsoye, F. Ilhane, N. Marzban, J. Proc. Safety Environ. Prot. 121 (2019) 103.

[4] E. Derakhshani, A. Naghizadeh, J. Mol. Liq. 259 (2018) 76.

[5] N. Bougdah, N. Messikh, S. Bousba, P. Magri, F. Djazi, R. Zaghdoudi, J. Chem. Eng. Trans. 60 (2017) 223.

[6] B. B. Mamba, R.W. Krause, T.J. Malefetse, S.P. Sithole, T.I. Nkambule, J. Water. Soil. Air. 35 (2009) 117.

[7] A. H. Chin, S. P. Yeap, J. Prog. Energy Environ. 6 (2018) 33.

[8] K. Y. A. Lin, H. A. Chang, J. Water. Air. Soil. Pollut. 226 (2015) 2280.

[9] Y. Lu, S. Hu, Z. Wang, Y. Ding, G. Lu, Z. Lin, Z. Dang, Z. Shi, J. Environ. Sci. Nano. 6 (2019) 747.

[10] A. Mehrparvar, A. Rahimpour, M. Jahanshahi, J. Taiwan. Inst. Chem. Eng. 45 (2014) 275.

[11] A. Rahimi, M. Kiralan, F. Ahmadi, J. Agric. Res. 9 (2020) 121.

[12] B.L. Rivas, E.D. Pereira, M. Palencia, J. Sánchez, J. Prog. Polym. Sci. 36 (2011) 294.

[13] A. Naz, A. Kausar, M. Siddiq, M.A. Choudhary, J. Polym. Plast. Technol. Eng. 55 (2016) 171.

[14] A. Naghizadeh, H. Shahabi, F. Ghasemi, A. Zarei, J. Water. Health. 14(6) (2016) 989.

[15] T.S. Chung, L.Y. Jiang, Y. Li, Prog. Polym. Sci. 32 (2007) 483.

[16] J. Wang, Y. Zhou, A. Li, L. Xu, J. Hazard. Mater. 2010; 176 (2010) 1018.

[17] P. Jin, J. Song, L. Yang, X. Jin, X.C. Wang, J. Environ. Pollut. 233 (2018) 290.

[18] Q. Tao, Z. Xu, J. Wang, F. Liu, H. Wan, S. Zheng, J. Microporous Mesoporous Mater. 131 (2010) 177.

[19] E. Eren, A. Sarihan, B. Eren, H. Gumus, F.O. Kocak, J. Membr. Sci. 475 (2015) 1.

[20] B. S. Lalia, V. Kochkodan, R. Hashaikeh, N. Hilal, Desalination. 326 (2013) 77.

[21] K. Irfana, K. Arun, M. Isloor, A.F. Ismail, Desal. Water Treat. 54 (2015) 1.

[22] L. L. Hwang, H. H. Tseng, J. C. Chen, J. Membr. Sci. 384 (2011) 72.

[23] M. Yao, J. Nan, Q. Li, D. Zhan, T. Chen, Z. Wang, H. Li, J. Membr. Sci. 495 (2015) 37.

[24] M. Amano, J. Lohwacharin, A. Dubechot, S. Takizawa, J. Environ. Manage. 212 (2018) 323.

[25] Y. H. Teow, A. L. Ahmad, J. K. Lim, B. S. Ooi, J. Appl. Polymer Sci. 128 (2013) 3184.

[26] M. Ebrahimi, S. Bagheri, M. Maleki Taleghani, M. Ghorabani, Desal. Water Treat. 152 (2019) 60.

[27] E. M. Pena Mendez, J. Havel, J. Patocka, J. Appl. Biomed. 3 (2005) 13.

[28] W. Zhang, H. Emamy, P. Betancourt, F. Vargas-Lara, J. F. Dougla, J. Chem. Phys. 151 (2019) 124705.

[29] B. Mombeni Goodajdar, F. Marahel, L. Niknam, E. Pournamdari, E. Mousavi, Int. J. Environ. Anal. Chem. 101(7) (2021) 1.

[30] M. Jemeljanova, R. Ozola, M. Klavins, J. Agr. Res. 17 (2019) 1023.

[31] S. Mallakpour, P. Asadi, Polym. Bull. 68 (2012) 53.

[32] S. M. Momeni, M. Pakizeh, Brazilian. J. Chem. Eng. 30 (2013) 589.

[33] M. G. Dawood, Y. R. Abdel-Baky, M. E. S. El-Awadi, G. S. Bakhoum, J. Front. Plant. Sci. 1 (2019) 28.

[34] M. Masoudzadeh, N. Karachi, J. Phys. Theore. Chem. 14(3) (2018) 259.

[35] M. Rahmani Piyani, M. Abrishamkar, B. Mombini Goodajdar, M. Hosseini sabzevari, J. Appl. Chem. Res. 16(1) (2022) 8.

[36] M. Salman, B. El-Eswed, F. Khalili, J. Appl. Clay. Sci. 38 (2007) 51.

[37] L. Rasuli, A.H. Mahvi, J. Water. Chem. Technol. 38 (2016) 21.

[38] F. Gomri, G. Finqueneisel, T. Zimny, S.A. Korili, A. Gil, M. Boutahala, J. Appl. Water. Sci. 8 (2018) 156.

[39] E. Niknam, A.A. Babaei, A. Ansari, Desal. Water. Treat. 92 (2017) 116.

[40] S. Bousba, N. Bougdah, N. Messikh, P. Magri, J. Phys. Chem. Res. 6 (2018) 613.

[41] L. N. Shiyan, K. I. Machekhina, E. N. Gryaznova, J. Mater. Sci. Eng. 110 (2016) 12097.

[42] G. Hasani, H. Daraei, B. Dhahrnoradi, F. Gharibi, A. Maleki, K. Yetilmersoy, G. Mc kay, J. Proc. Safety Environ. Prot. 117 (2018) 111.

[43] A. Naghizadeh, S. Nasseri, A. H. Mahvi, R. Nabizadeh, R. R. Kalantary, Desal. Water Treat. 54 (2015) 2490.

حذف اسیدهای هیومیک از محلول‌های آبی با کمک اولتراسونیک روی غشای ماتریس مخلوط پلی‌سولفون/Fe_2O_3 به روش اولتراسونیک، یک روش طراحی تجربی ۱

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چکیده

در مطالعه حاضر، کاربرد سنتز غشای ماتریس **پلی سولفون**/Fe_2O_3 برای حذف سریع اسید هیومیک از محلول های آبی. تکنیک های یکسانی از جمله FT-IR، XRD و SEM برای توصیف این ماده جدید استفاده شده است. بررسی قابلیت کاربرد غشاء ماتریکس مخلوط **پلی سولفون**/Fe_2O_3 را به عنوان یک جاذب در دسترس، مناسب و کم هزینه برای حذف مناسب اسید هیومیک از محیط های آبی نشان داد. همچنین تأثیر متغیرهایی از جمله غلظت اولیه اسیدهای هیومیک (X1)، pH (X2)، دوز جاذب (X3)، زمان فراصوت (X4) با استفاده از طراحی مرکب مرکزی (CCD) تحت روش سطح پاسخ (RSM) مورد بررسی قرار گرفت.). علاوه بر این، تأثیر pH محلول، مقدار نانوذرات، غلظت اسیدهای هیومیک و زمان تماس مورد بررسی قرار گرفت. آزمایش‌ها با استفاده از روش سطح پاسخ طراحی شده‌اند. در این مقاله مقادیر ۱۲ میلی گرم در لیتر، ۰/۰۳۰ گرم، ۷/۰، ۴/۰ دقیقه به ترتیب به عنوان مقادیر ایده آل برای غلظت اسید هیومیک ، جرم جاذب، مقدار pH و زمان تماس در نظر گرفته شد. مطالعات سیتیک و ایزوترم مناسب بودن مدل های مرتبه دوم و لانگمویر را برای سیتیک و ایزوترم جذب اسیدهای هیومیک روی جاذب ثابت کرد. ثابت شد که جاذب برای بیش از یک بار قابل بازیافت است. از آنجایی که تقریباً ۹۹/۵ درصد از اسیدهای هیومیک با ظرفیت جذب ایده آل (۱۰۵/۰ میلی گرم در گرم) برای اسید هیومیک حذف شد. نتایج کلی تأیید کرد که غشای ماتریس مخلوط **پلی سولفون**/Fe_2O_3 می‌تواند یک ماده جاذب امیدوارکننده برای حذف اسیدهای هیومیک از محلول‌های آبی باشد.

کلید واژه‌ها: اسیدهای هیومیک (HAs)؛ ظرفیت جذب؛ غشاهای ماتریس مخلوط پلی سولفون/Fe_2O_3؛ روش سطح پاسخ (RSM)؛ طراحی مرکب مرکزی (CCD)..

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