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Removal of Humic Acids (HAs) in Drinking Water by Adsorption onto Polysulfone/Fe_2O_3 Mixed Matrix Membrane: Study kinetics and Isotherm Analysis

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Abstract

The present study delineates the applicability of polysulfone/ X% Fe_2O_3 mixed matrix membranes as a low-cost and non-toxic natural adsorbent. It was used to remove humic acids (HAs) rapidly from aqueous solutions. The polysulfone/ X% Fe_2O_3 mixed matrix membranes were characterized by BET, FT-IR, XRD, and SEM. The humic acids (HAs) removal by the developed adsorbent was investigated using the batch adsorption technique and all parameters influencing the removal efficiency such as dose of adsorbent and pH were considered. The optimal conditions for the humic acids (HAs) removal were found to be 5, 120-160 min, 10 mg/L, and 0.1 g for pH, contact time and adsorbent dosage respectively. The rapid adsorption of the humic acids (HAs) is an advantage of this adsorbent. The adsorption capacity of humic acids (HAs) onto polysulfone/ X% Fe_2O_3 mixed matrix membrane was reasonably constant in the pH range of 5–7 but decreased as the pH exceeded 5. Various isotherm models were used to fit the experimental equilibrium data. Equilibrium data obtained have been fitted to the Langmuir, Freundlich, and Dubinin–Radushkevich adsorption isotherms. Langmuir's model best fits the experimental results. Kinetic modeling showed that the pseudo-second-order equation was the most appropriate for the description of humic acids (HAs) for PSF, PSF/5% Fe_2O_3, and PSF/10% Fe_2O_3 mixed matrix membrane were found to be 13.333, 10.309, and 7.874 mg/g, respectively. The overall results confirmed that polysulfone/ X% Fe_2O_3 mixed matrix membrane could be a promising adsorbent material for humic acids (HAs) removal from aqueous solutions.

Keywords: Adsorption, Humic acids (HAs), Kinetic, Polysulfone/ X% Fe_2O_3 mixed matrix membrane.

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Introduction

Disinfection is a process in which infective organisms or pathogenic micro-organisms are removed or deactivated. Water disinfection is performed before its distribution to make drinking water supplies safe and free of the pathogen [1]. However, the most important problem caused by such substances is their contribution as a precursor to the production of disinfection by-products (DBP). For this reason, more disinfectant is used in the process so that the risk of the formation of DBP increases despite increased disinfection efficiency. They have no specific smell in water but are physiologically associated with health hazards such as gene mutation and cancer [2]. Humic substances (mainly humic acids and fulvic acids) are present in almost all natural waters and often represent a major proportion of organic pollution (known in the literature as natural organic matter-NOM) [3]. 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 [4]. Humic acid may cause water to have an undesirable taste and color. Moreover, 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 [5]. The factors that determine the composition of humic substances are location dependent and include the source of the organic matter, the water chemistry, temperature, pH, and biological processes, and the elementary composition of humic substances [6].

Since 1974, several epidemiological surveys have confirmed the correlation between a variety of cancers in humans and animals and drinking of or contact with the chlorinated water. Humic acids (HAs) as the main chlorine disinfection by-products are toxic, carcinogenic, and mutagenic [7]. The presence of organic compounds in water resources provokes numerous troubles during treatment processes specifically if conventional water treatments are practiced. NOM can affect water treatment and the leading effect of these materials is the creation of chlorination by-products due to their reaction with chlorine. The direct relationship between the formation of chlorination by-products and the concentration of NOM as the most important precursor in the formation of these compounds has been confirmed. Only 30% of NOM precursors have been removed in the conventional water treatment processes [8]. Humic substances belong to a class of organic compounds with high molecular weight and an aromatic aliphatic character which contain carbon, oxygen, hydrogen, nitrogen and sulfur. The reported relative molecular weight of humic substances is from a few hundred to millions of daltons. Location-dependent factors like the source of the organic matter, water chemistry, temperature, pH, and biological processes [9] are among the factors that ascertain the composition of humic substances. By surveying the chemical characteristics of humic substances, the presence of carboxylic acid and the hydroxy (phenol, alcohol), methoxy, and carbonyl groups can be specified that along with the aliphatic side chains are bound to the nucleus [10]. Carcinogenicity and toxicity of these substances have been confirmed [10]. 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 major proportion of organic contaminations (known in the literature as natural organic materials – NOM) [11].

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]. Polymer NCs incorporates the remarkable features of both nanoparticles (NPs) and polymers: the unique physical and chemical properties resulting from the large surface area to volume ratios, the high interfacial reactivity of nanofillers, and outstanding mechanical properties and compatibility owing to their polymer matrix, being also amenable to regeneration and reuse [14,15].

In the last decades, several NCs have been fabricated for the adsorptive removal of heavy metals from water and wastewater [16]. Overall, various effects contribute to determining the whole efficacy of NCs action. The composite matrix can be aromatic polyamides (PA). Aromatic Pas are well-known as high-performance polymers because of they combined excellent thermal, mechanical, and chemical properties that make them useful in applications for advanced technologies [17]. Recently, blending of the polymers with inorganic nanomaterials has occupied an impressive platform of research because of their simplicity, stable performance, and mild operating conditions [18]. The addition of NPs to the polymer matrix has been the most usually accepted technique for manufacturing polymer NCs and the hybrids prepared with a uniform dispersion of NPs can offer good mechanical strength, antifouling or self-cleaning, bactericidal, and also to some extent, photocatalytic properties [19] 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 [20]. Using effective, non-toxic, and low-cost adsorbents along with simple design and ease of operation made this technique beneficial and popular. The appropriateness of the adsorbent depends on factors such as elimination capacity, treatment cost, and operating conditions [21]. Therefore, for the elimination of humic acids (HAs) and their precursors, it is essential to exercise suitable methods. Amongst the variety of methods, the adsorption process as a simple and standard method is considered advantageous for the elimination of organic pollutants like humic acid. Activated carbon, in theory, is the best adsorbent for humic acids (HAs) elimination, however; in practice, it exhibits a low capacity for the elimination of high molecular organic compounds such as NOM [22].

Chemical treatment and biodegradation procedures are not only based on expensive and complex processes but also produce noxious by-products. On the other hand, the elimination of humic acids (HAs) based on biological treatment and chemical precipitation has low efficiency and is not environmentaly friendly [23, 24]. Therefore, preparing polysulfone/ Fe_2O_3 membrane as an alternative to exorbitant or noxious adsorbents for the elimination of humic acids (HAs) from wastewater attracted our attention. To characterize this adsorbent, X-ray diffraction pattern and FTIR of the polysulfone/Fe2O3 membrane were employed. Investigating and optimizing the experimental conditions including pH of the solution, initial humic acids (HAs) concentration, contact time, and adsorbent dosage as well as the humic acids (HAs) removal percentage as a response was performed. Also, the investigation about the extent to which the experimental factors interact with each other was performed. The optimal conditions for the humic acids (HAs) elimination for pH, contact time, initial humic acids (HAs) concentration, and adsorbent dosage were estimated to be 5, 120-180 min, 10 mg/L and 0.1g respectively. To best fit the experimental equilibrium data, different isotherm models like Langmuir, Freundlich, and Dubinin–Radushkevich were employed. The obtained outcomes demonstrated the appropriateness and pertinence of the Langmuir model and the fitness and relevance of the Dubinin–Radushkevich model were proven by the obtained outcomes. By applying the kinetic models of pseudo-first-order, pseudo-second-order and Elovich diffusion models, it was shown that the pseudo-second-order model regulates the kinetics of the adsorption process. The effective use of the polysulfone/ X% Fe_2O_3 mixed matrix membranes to eliminate the humic acids (HAs) from wastewater was confirmed.

Experimental

Preparation of Stock Solution

All chemicals were of reagent grade and used without further purification. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used for the pH adjustment. 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 [25].

Instrumentation

UV–vis spectrophotometer (Jasco, Model UV–vis V-530, Japan) and 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 [26].

Preparation of pure polysulfone/X%Fe_2O_3 mixed matrix membrane

The synthesis of pure and polysulfone/ X% Fe_2O_3 mixed matrix membrane nanoparticles was carried out at room temperature by the precipitation method. In this procedure, to obtain a homogeneous mixture of PSF/m-Fe_2O_3 composites with different amounts of m-Fe_2O_3 NPs (0, 5, 10, and 15 wt %), a two-step process was used. At first, two solutions were synthesized: 0.1 g of polymer was dissolved in 2 mL DMSO and m-Fe_2O_3 was separately dispersed in 2 mL DMSO solution with stirring for 24 h at $25^{°C}$. Then, the solutions were mixed to reach the preferred weight percentages of m-Fe_2O_3 from 5 to 15 wt %. The PSF/ m-Fe_2O_3 solutions were stirred for 24 h at $25^{°C}$ and then it was sonicated for 2 h in an ice bath with a frequency of 2.259×10^4 Hz and power 100 W. To remove the solvent, obtained PSF/ m-Fe_2O_3 solutions were poured into glass Petri dishes and after 24 h at ambient temperature, PSF/ m-Fe_2O_3NCs were prepared. The solution was stirred well with the help of a 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_2O_3. The reactive solution was continuously stirred for 2 h. The powder was collected and dried in a hot air oven at 57^{oC}. The resulting mixture was washed several times and dried in an oven leading to the synthesis of polysulfone/ X% Fe_2O_3 mixed matrix membranes.

Adsorption of humic acids (HAs) onto polysulfone/X%Fe_2O_3 mixed matrix membranes

A batch process using polysulfone/ X% Fe_2O_3 mixed matrix membranes was applied for binary adsorption of humic acids (HAs) while all experiments were undertaken in a cylindrical glass vessel by adding 0.1g of adsorbent to 100 ml of PH 5.0 for humic acids (HAs) as optimum value. The vessel was immersed in bath for 120-160 min at room temperature and subsequently, the solutions were centrifuged. Then non-adsorbed dye contents were determined by using UV–Vis spectrophotometer set at wavelengths 480 nm for humic acids (HAs) respectively [27].

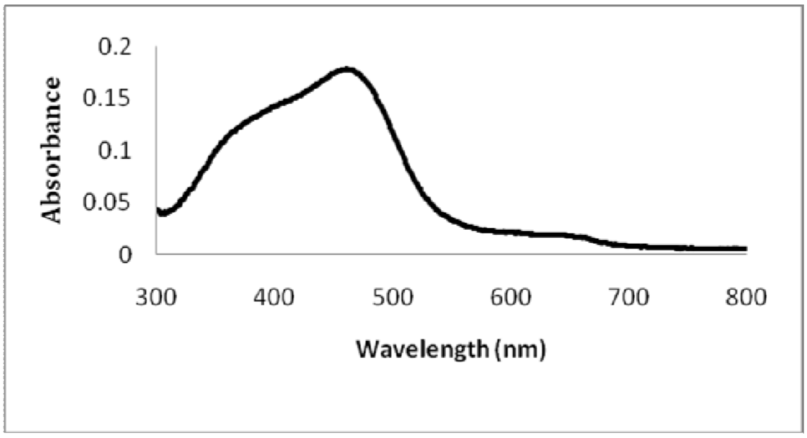

Figure 1. Physisorption isotherm of humic acids (HAs) into polysulfone/ X% Fe_2O_3 mixed matrix membranes.

Batch adsorption humic acids (HAs) adsorption process

Batch adsorption experiments were carried out to determine the humic acids (HAs) adsorption isotherm onto polysulfone/ X% Fe_2O_3 mixed matrix membrane and its thermodynamic properties: 100 mL solution having 10 mg/L concentration of humic acids (HAs) were prepared and Initial pH of the solution was adjusted with the help of 0.01N HCl / 0.01N NaOH aqueous solution without any further adjustments during the experiments. 10 samples of 50 mL solution were taken in ten 100 mL flasks containing a fixed adsorbent dose of 10 mg/L. These flasks were agitated at a constant rate of 180 rpm in a temperature-controlled orbital shaker maintained at 25^{oC} temperatures. One of the samples after fixed time intervals (20 at 240 min) and analyzed for remaining humic acids (HAs) was present in the adsorbate solution. Polysulfone/X% Fe_2O_3 mixed matrix membrane was separated from an aqueous solution by filtration through Whatman No. 42 filter paper. The humic acids (HAs) concentration in the solution was measured using a double beam UV–vis spectrophotometer (Jasco, Model UV–vis V-530, Japan) set at wavelengths 480 nm for humic acids (HAs). The amount of adsorbed humic acids (HAs) at equilibrium (qe(mg/g)) was calculated using the equation:

$$\%A=\frac{C_0-C_e}{Ct}\times 100 \qquad (1)$$

Where $C_\circ(mgL^{-1})$ and $C_t(mgL^{-1})$ is the concentration of target at initial and after time t respectively.

$$q_e=\frac{(C_\circ-C_e)V}{W} \qquad (2)$$

where $C_{\circ}(mgL^{-1})$ and $C_e(mgL^{-1})$ are the initial humic acids (HAs) concentration and equilibrium humic acids (HAs) concentration in aqueous solution, respectively, V (L) is the solution volume and W (g) is the adsorbent mass.

Results and discussion

Characterization of adsorbent pure polysulfone/X%Fe_2O_3 mixed matrix membrane

The nitrogen adsorption–desorption isotherm at 77 K onto Pure polysulfone/ X% Fe_2O_3 mixed matrix membrane is shown in Table.1, which is in correspondence with classical type II isotherm of IUPAC classification [28]. According to the results of the BJH method, the average specific surface area and total pore volume of pure polysulfone/ X% Fe_2O_3 mixed matrix membrane were 96 m^2/g and 3.36×10^{-2} cm^3/g, respectively. The adsorption capacity of pure polysulfone/ X% Fe_2O_3 mixed matrix membrane depends on the porosity and chemical reactivity of functional groups at the surface. Knowledge on surface functional groups would give insight into the adsorption capability of the pure polysulfone/ X% Fe_2O_3 mixed matrix membranes.

Figure 2 shows the N2 adsorption–desorption isotherms and pore size distributions. The nitrogen sorption isotherms of Polysulfone/Fe_2O_3NPs exhibited typical type II isotherm, which is characteristic of mesoporous materials.

Table. 1. Characterization of Polysulfone and BET analysis of Polysulfone/Fe_2O_3NPs.

		Samples	
		Polysulfone	Polysulfone/Fe_2O_3NPs
	Surface area (m^2/g)	81.4	100.8
	Correlation Coefficient	0.994	0.991
BJH adsorption summary	Surface area (m^2/g)	96.25	96.11
	Pore volume (m^3/g)	3.48×10^{-2}	3.36×10^{-2}
	Pore diameter (nm)	8.4	8.1
BJH desorption summary	Surface area (m^2/g)	117.32	109.23
	Pore volume (m^3/g)	3.52×10^{-2}	3.34×10^{-2}
	Pore diameter (nm)	9.5	9.2

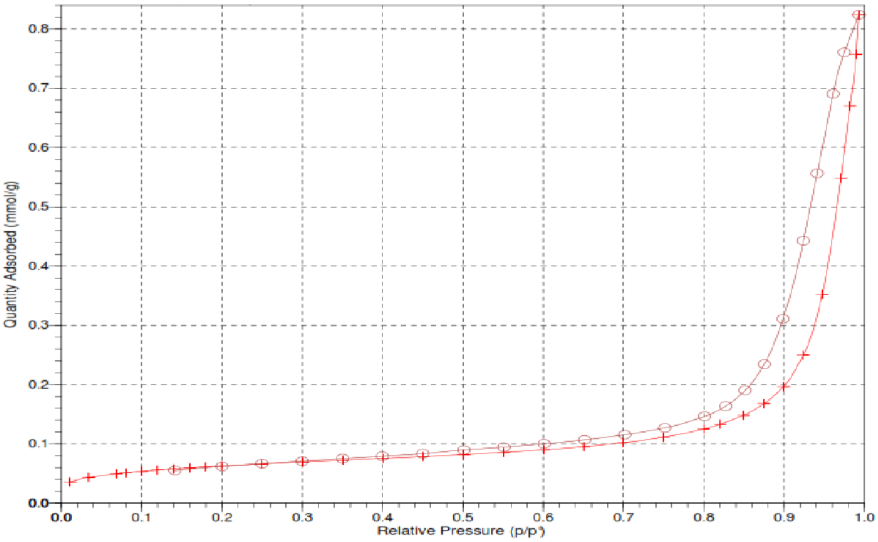

Figure 2. Nitrogen adsorption–desorption isotherms of Polysulfone/Fe_2O_3NPs.

FTIR analysis

FTIR spectra for pure polysulfone/ X% Fe_2O_3 mixed matrix membrane (x = 10%) are shown in Fig. 3. The vibrational frequencies for stretching bonds in PSF membrane molecules cannot be detected by FTIR analysis. This confirms that PbS does not 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 FTIR spectra of pure and polysulfone/ X% Fe_2O_3 mixed matrix membranes is observed [29].

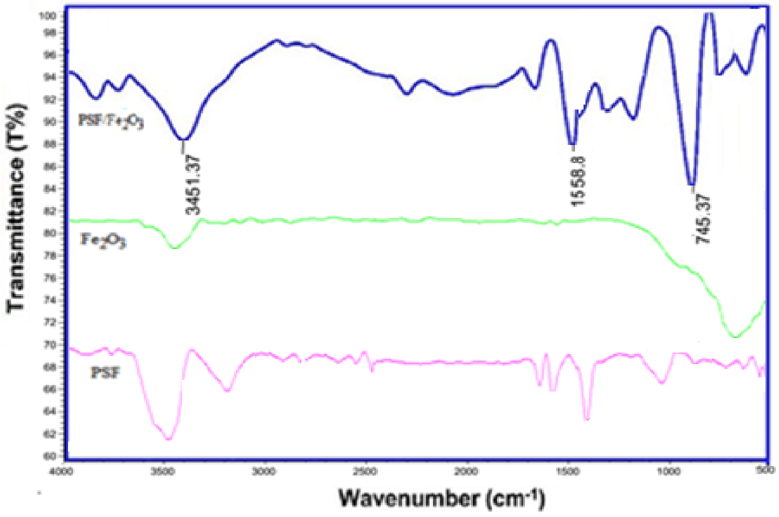

Figure 3. FTIR spectra of pure polysulfone/ X% Fe_2O_3 mixed matrix membrane.

XRD analysis

The XRD pattern of the pure and polysulfone/ X% Fe_2O_3 mixed matrix membrane is shown in Fig. 4. The synthesized nanopowders are found to be polycrystalline. 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_2O_3 mixed matrix membrane respectively (JCPDS no. 78–1901) [30].

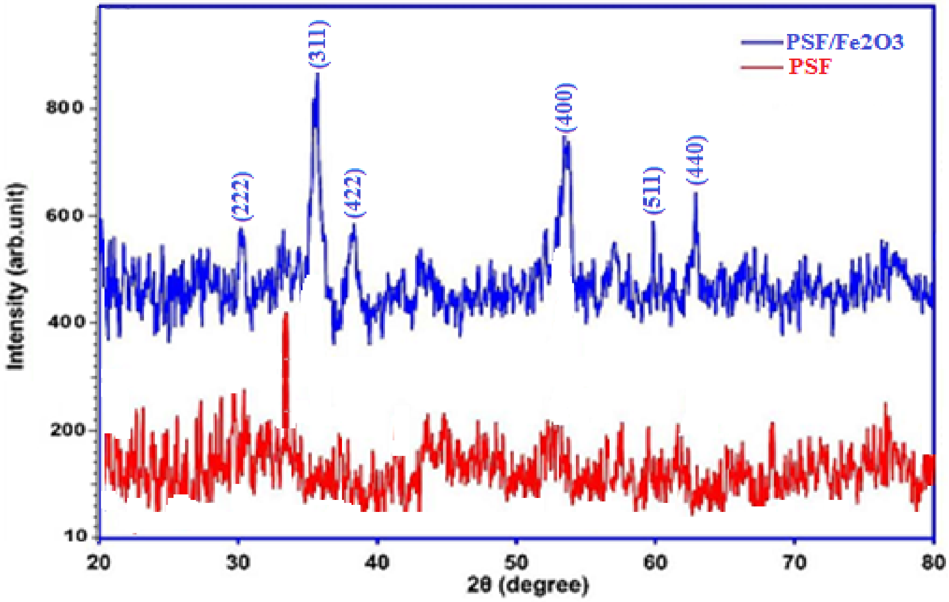

Figure 4. The XRD patterns of polysulfone/ X% Fe_2O_3 mixed matrix membrane (x = 0%, 5% and 10%).

Surface morphology

The graph in Fig.5 shows the morphological features and particle size distribution of the polysulfone/ X% Fe_2O_3 mixed matrix membranes (x=10%) using the SEM micrograph. It has been seen that the particles were mostly spherical with various size distributions as they form agglomerates. From the particle size distribution, we obtain the average particle size in the range of 35-60 nm very close to those determined by XRD analysis [31].

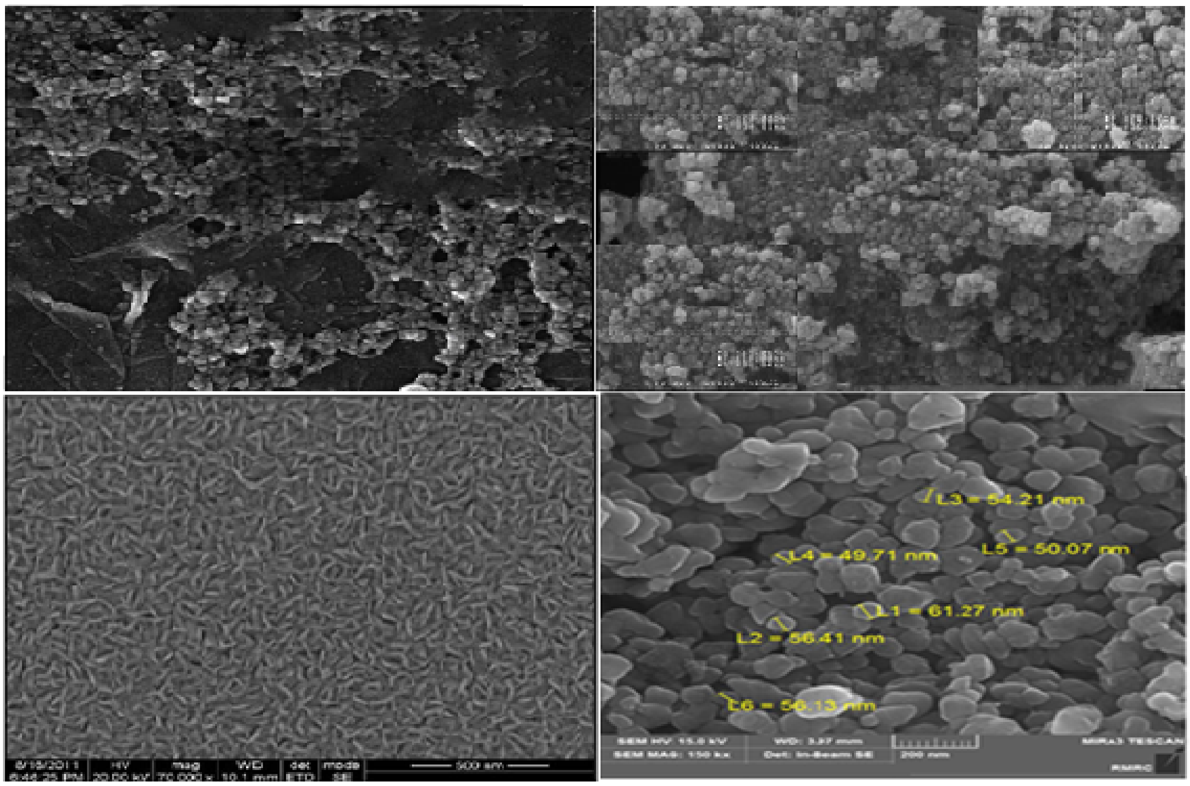

Figure 5. The (SEM) image of the prepared polysulfone/ X% Fe_2O_3 mixed matrix membranes.

Effect of pH on the adsorption of humic acids (HAs)

The pH value plays a very important role in the adsorption process (Fig.6) and shows the removal of humic acids (HAs) as a function of pH at different sorbents. To control optimum pH for the maximum elimination of humic acids (HAs), the equilibrium adsorption of humic acids (HAs) was measured at different pH levels from 2.0 to 7.0 by setting the initial humic acids (HAs) concentrations at 10 ppm and the results are summarized in Table.2 [32]. The maximum removal percentages of humic acids (HAs) are obtained at pH = 5.0 for pure PSF, PSF/5% Fe_2O_3, and PSF/10% Fe_2O_3 mixed matrix membrane at 78.3, 84.2, and 87.4% respectively [33].

Table. 2. Adsoption quality and distribution coefficient parameters for humic acids (HAs) solution (10 mg L^{-1}, pH= 5), onto polysulfone/ X% Fe_2O_3 mixed matrix membranes.

Sample	HAs contect solution (mg/L)		Removal efficiency (%)	Kd (mLg^{-1}) 10^3	q_e
	Initial (Ci)	Final (Ce)			
PSF/10% Fe_2O_3 membrane	10	2.17	78.3	3.132	6.796
PSF/5% Fe_2O_3 membrane	10	1.58	84.2	3.368	5.321
PSF membrane	10	1.26	87.4	3.496	4.405

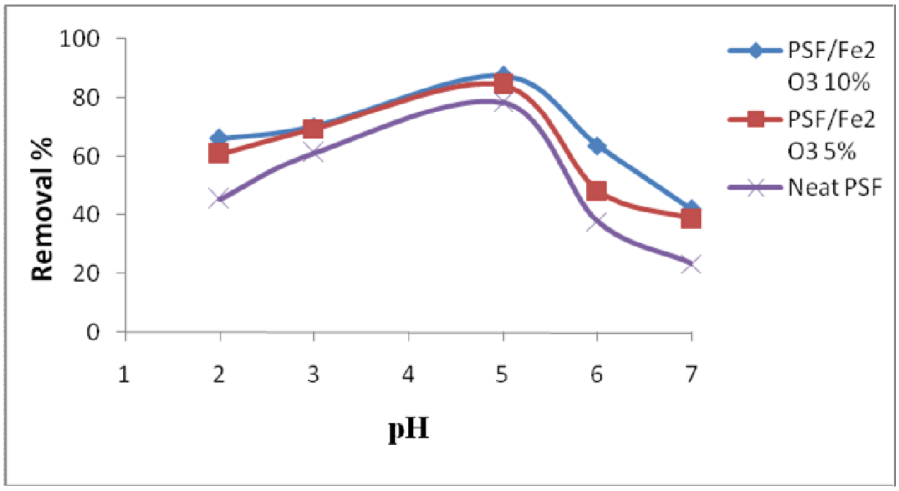

Figure 6. Effect of pH on humic acids (HAs) removal [HAs conc =10 mgL^{-1}; adsorbent dose = 0.1g L^{-1}; contact time = 150 min; stirring speed = 180 rpm; temp = 25°C].

Effect of the contact time on the adsorption of humic acids (HAs)

Figure 7 indicates the effect of contact time on sorption of humic acids (HAs) by synthesized PSF, PSF/5% Fe_2O_3, and PSF/10% Fe_2O_3 mixed matrix membrane. It is observed that there is little change of sorption rate at 120, 140, and 160 min for pure PSF, PSF/5% Fe_2O_3 and PSF/10% Fe_2O_3 mixed matrix membrane respectively and leveled off gradually until the humic acids (HAs) adsorption showed no considerable increasing and the removal finally reached equilibrium [34]. Therefore, the maximum removal percentages at contact time 160, 140 and 120 min for pure PSF, PSF/5% Fe_2O_3 and, PSF/10% Fe_2O_3 mixed matrix membrane are respectively 88.4%, 83.6%, and 73.5%.

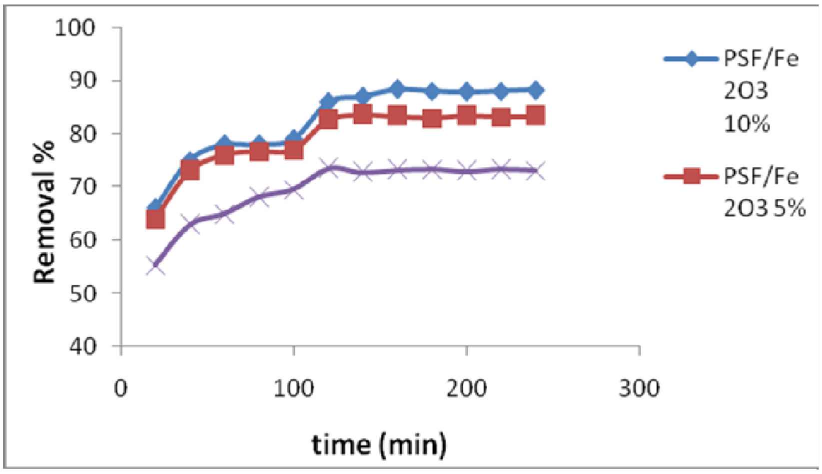

Figure 7. Effect of time on humic acids (HAs) removal [HAs conc = 10 mg L^{-1}; pH=5.0; contact dose adsorbent = 0.1 g; stirring speed= 180 rpm; temp= 25^{oC}].

Effect of Temperature

Figure 8 shows the effect of temperature on the adsorption of humic acids (HAs). From the results it is evident that there is a gradual increase in the removal percentage from 68.8% to 87.0% for pure PSF/10% Fe_2O_3 mixed matrix membrane, 63.0% to 81.4% for pure PSF/5% Fe_2O_3 mixed matrix membrane and 59.0% to 76.0% for pure PSF membrane. The above results also showed that the adsorption was endothermic in nature. Since the adsorbent is porous in nature and the possibilities of diffusion of adsorbate cannot be ruled out, the increase in the sorption with the rise of temperature may be diffusion controlled which is endothermic process, the rise of temperatures favors the adsorbate transport with in the pores of adsorbent [35].

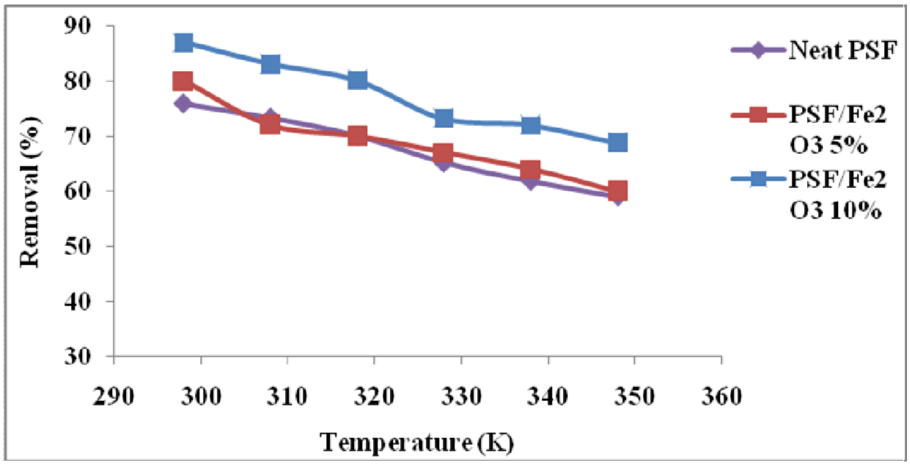

Figure 8. Effect of temperature on humic acids (HAs) removal [HAs conc = 10 mg L^{-1}; adsorbent dose = 0.1g L^{-1}; pH = 5.0; contact time = 150 min, stirring speed = 180 rpm].

Biosorption isotherms

An adsorption isotherm describes the fraction of sorbate molecules that are partitioned between liquid and solid phases at equilibrium. Adsorption of humic acids (HAs) onto pure PSF, PSF/5% Fe_2O_3, and PSF/10% Fe_2O_3 mixed matrix membrane was modeled using four adsorption isotherms: Langmuir, Freundlich, and Dubinin-Radushkevich isotherms [36].

Adsorption equilibrium study

The equilibrium relationship is based on the mathematical connection of an established equilibrium between the quantity of adsorbed target per gram of adsorbent (q_e(mg/g)) and the equilibrium non-adsorbed quantity of ions in solution (C_e (mg/L) at a specified temperature is defined by adsorption equilibrium isotherms [37,38]. By using 3 models of Freundlich adsorption isotherm, Langmuir adsorption isotherm, and Dubinin–Radushkevich (D-R) isotherms, the adsorption isotherm of adsorption was evaluated.

1) In Langmuir adsorption isotherm no interaction amongst adsorbed molecules and the adsorption process occurred on uniform surfaces. The ensuing equation presents the Langmuir model clearly [39]:

$$C_e/q_e = 1/K_L q_{max} + C_e/q_{max}$$

Where C_e (mg/L), q_e (mg/g), and q_{max} (mg/g) signify the equilibrium concentration, the adsorption capacity, and the maximum adsorption capacity of the adsorbents in the aqueous solution. The Q_m (mg g^{-1}) values of humic acids (HAs) were 7.874, 10.309, and 13.333 for pure PSF, PSF/5% Fe_2O_3, and PSF/10% Fe_2O_3 mixed matrix membranes respectively. K_L is a constant related to the binding energy of the sorption system (L/mg) (Figure 9).

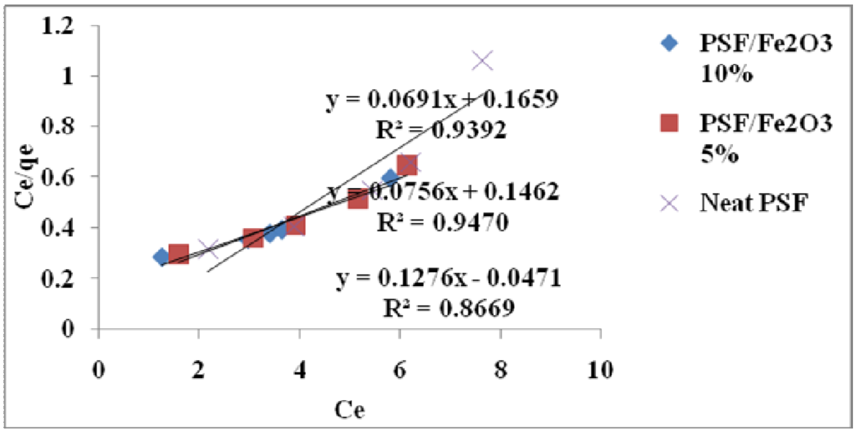

Figure 9. Langmuir isotherm for the adsorption of humic acids (HAs) [pH =5.0; adsorbents dose = 0.1 g L^{-1}; temperature = 25°C].

2) Freundlich adsorption isotherm: This model can be explained the multilayer adsorption of adsorbate onto a heterogeneous surface of an adsorbent. The linear form of Freundlich isotherm model expression is given as:

$$\text{Log } q_e = \log k_f + 1/n \log Ce$$

That K_f (the adsorption capacity) and n (intensity of a given adsorbent) are the Freundlich isotherm constant (Figure 10).

The values of the constants in both models are obtained from the slope and the position (Fig. 10). Table 3 shows the results of the fit and of the constants of both models for humic acids (HAs). The Q_m (mg g^{-1}) values of humic acids (HAs) for pure PSF, PSF/5% Fe_2O_3, and PSF/10% Fe_2O_3 mixed matrix membranes were 4.667, 5.715, and 6.982 respectively. The values between 1 and 10 for n in the adsorption process are favorable [40]. All the correlation coefficients and parameters obtained for the isotherm models from (Table 3) reveal that the Langmuir isotherm is the best model to demonstrate the adsorption of humic acids (HAs) for pure PSF, PSF/5% Fe_2O_3, and PSF/10% Fe_2O_3 mixed matrix membranes adsorbent.

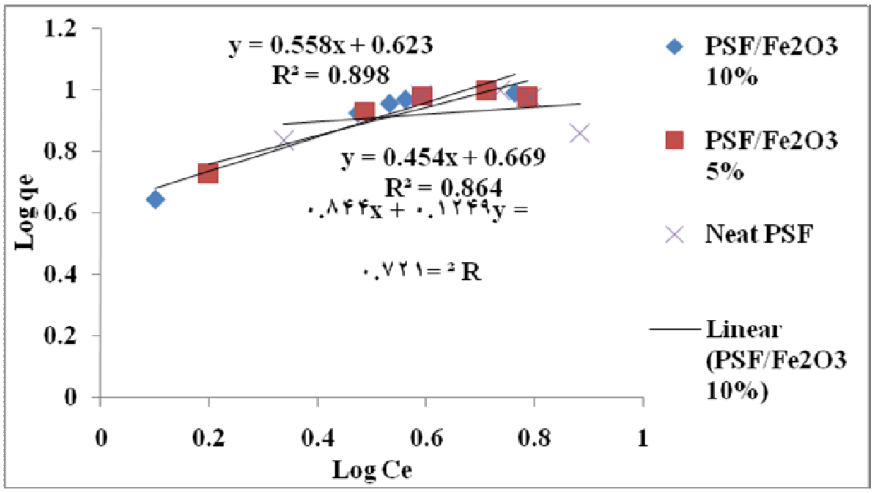

Figure 10. Freundlich isotherm for the adsorption of humic acids (HAs) [initial HAs conc = 10 mg L-1; pH = 5.0; adsorbents dose = 0.1 g L^{-1}; temperature = 25°C].

3) To analyze the nature of adsorption, Dubinin–Radushkevich (D-R) isotherm model is utilized. In the ensuing equation, the linear form of this model is introduced:

$$Lnq_e=lnq_m-\beta\varepsilon^2 \qquad (7)$$

β in the foregoing formula stands for the activity coefficient relative to mean sorption energy (mol^2/kJ^2), and ε refers to the Polanyi potential which is calculable by the following equation:

$$\varepsilon = RTln(1+1/Ce) \qquad (8)$$

In the foregoing formula R stands for the ideal gas constant (8.3145 J/mol K) and T for absolute temperature (K) (Fig. 13d). E_a refers to the free energy change of adsorption (kJ/mol) which stands in need of transferring 1 mol of ions from solution to the adsorbent surface and is calculable by the ensuing equation [41]:

$$E_a = 1/(-2\beta)^{1/2} \qquad (9)$$

In this model, the mechanism of adsorption is considered Physical if Ea is smaller than 8 kJ/mol but if E_a is greater than 20 kJ/mol, the mechanism of adsorption is considered to be chemical and finally if $8 > E_a < 20$ kJ/mol, the dominancy of chemical ion exchange in the adsorption is confirmed [42]. The Q_m (mg g^{-1}) values 4.18, 6.05 and 11.80 for pure PSF, PSF/5% Fe_2O_3 and PSF/10% Fe_2O_3 mixed matrix membranes respectively. This suggests that humic acids (HAs) adsorption for pure PSF, PSF/5% Fe_2O_3 and PSF/10% Fe_2O_3 mixed matrix membranes adsorbent is physical adsorption.

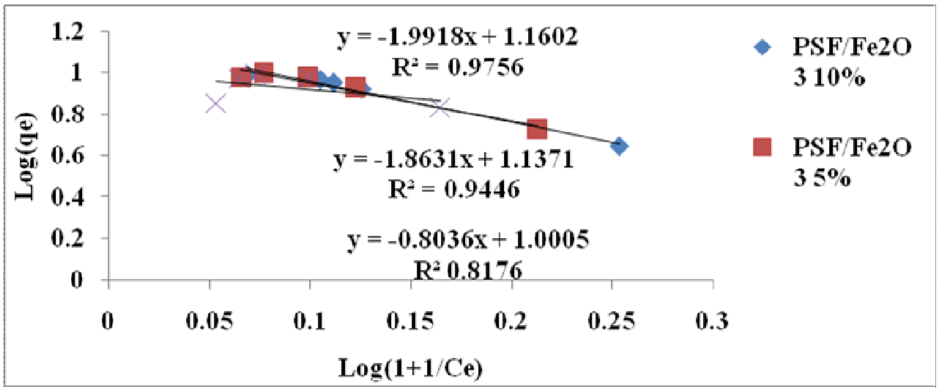

Figure 11. Dubinin-Radushkevich isotherm for the adsorption of humic acids (HAs) [initial HAs conc = 10 mg L^{-1}; pH = 5.0; adsorbents dose = 0.1 g L^{-1}; temperature = 25°C].

Table 3. Various isotherm constants and correlation coefficients calculated for the adsorption of humic acids (HAs) for pure PSF, PSF/5% Fe_2O_3 and PSF/10% Fe_2O_3 mixed matrix membranes.

Isotherm	**Equation**	**Parameters**	**Value of parameters For and PSF/10% Fe_2O_3 mixed matrix membranes**	**Value of parameters For PSF/5% Fe_2O_3 mixed matrix membranes**	**Value of parameters For pure PSF membranes**
Langmuir	$q_e=q_m bC_e/(1+bC_e)$	Q_m (mg g^{-1})	13.333	10.309	7.874
		K_L (L mg^{-1})	0.514	1.386	2.702
		R^2	0.947	0.930	0.866
Freundlich	$\ln q_e = \ln K_F + (1/n) \ln C_e$	n	2.203	3.534	8.064
		K_F $(mg)^{1-n}$ $L^n g^{-1}$	4.667	5.715	6.982
		R^2	0.8989	0.8641	0.7216
Dubinin-Radushkevich (DR)	$\ln q_e = \ln Q_d - B\varepsilon^2$	Q_m (mg g^{-1})	11.80	6.05	4.18
		E (kj mol^{-1})	-817.12	-770.1	-700.0
		R^2	0.9756	0.9446	0.8176

The adsorption kinetic studies

In an aqueous medium, adsorption of a solute by a solid is performed via complex stages [43]. Numerous parameters relative to the state of the solid (generally with the very non-uniform reactive surface) and physicochemical conditions under which the adsorption is taking place can affect the adsorption. Four kinetic models of 1-pseudo-first-order, 2- pseudo-second-order and 3-Elovich were applied to the data to evaluate the adsorption kinetics of metals [44]. The adsorption kinetic data were described by the Lagergren pseudo-first-order model [45]. The following formula introduces the Lagergren:

$$\frac{dq_t}{dt}=k_1(q_e-q_t)$$

1) The pseudo-first-order model that is shown in the equation below:

$$\ln(q_e - q_t) = \ln q_e - K_1 t$$

That K_1 is the rate constant of adsorption (min^{-1}) q_e and q_t are the amounts of humic acids (HAs) adsorbed per unit mass of the adsorbent ($mg\ g^{-1}$) at equilibrium and time t, respectively and were calculated according to:

$$q_e = (C_i - C_e)\ V/m$$
$$q_t = (C_i - C_t)\ V/m$$

Where C_t ($mg\ L^{-1}$) is the humic acids (HAs) concentrations at time t (Figure 12).

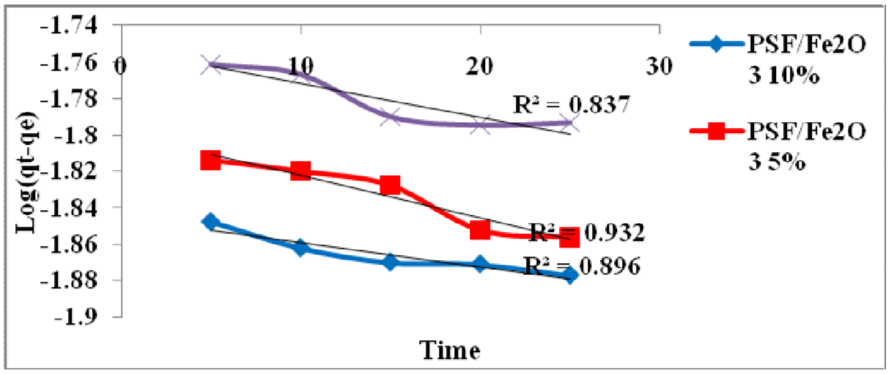

Figure 12. Pseudo-first order model for humic acids (HAs) adsorption [initial HAs conc = 10 mg L^{-1}; contact time = 150 min).

2) The pseudo-second-order model is expressed by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_{ad} q_e^2} + \frac{1}{q_e} t$$

That k_{ad} is the rate constant of equation (g mg^{-1} min^{-1}) and it can be calculated from the plots of t/q_t versus t. and h= k_{ad} q_e^2 (mg g^{-1} min^{-1}) Figure 13.

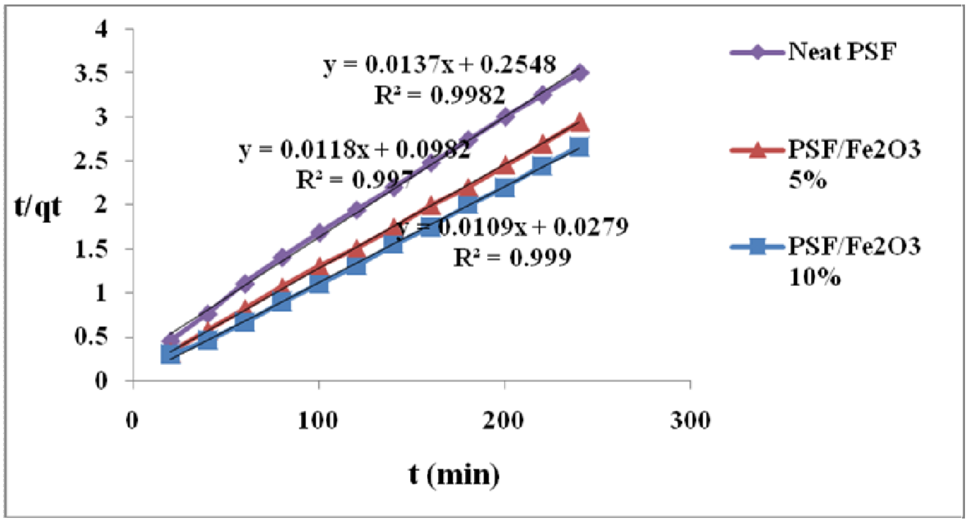

Figure 13. Pseudo-second order model for humic acids (HAs) adsorption [initial HAs conc = 10 mg L^{-1}; contact time = 150 min).

3) Elivich equation expression is given as:

$$q_t = \frac{\ln(hB)}{B} + \frac{\ln(t)}{B}$$

Where β is the desorption constant (mg g^{-1} min^{-1}) (Figure 14).

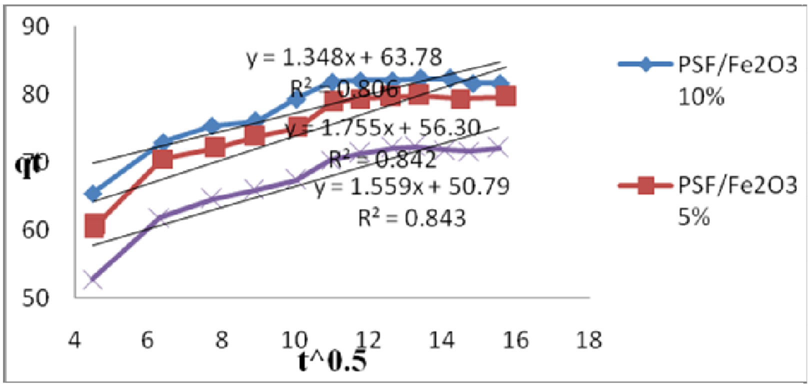

Figure 14. Elovich model for humic acids (HAs) adsorption [initial HAs conc = 10 mg L^{-1}; contact time = 150 min).

The correlation coefficient (R^2) values of the four kinetic models and other related kinetic parameters were calculated and listed in Table 4. Based on the values of the correlation coefficient

(R^2), it was found that the pseudo-second-order kinetic model has the highest matching with the experimental data than the other models for interpretation of adsorption mechanism of humic acids (HAs) for pure PSF, PSF/5% Fe_2O_3 and PSF/10% Fe_2O_3 mixed matrix membranes [47].

Table 4. Comparison of the Kinetic parameters for the Removal of humic acids (HAs) for pure PSF, PSF/5% Fe_2O_3 and PSF/10% Fe_2O_3 mixed matrix membranes.

Model	parameters	Value of parameters For and PSF/10% Fe_2O_3 mixed matrix membranes	Value of parameters For PSF/5% Fe_2O_3 mixed matrix membranes	Value of parameters For pure PSFmembranes
pseudo-First-order kinetic $\log(q_e - q_t) = \log(q_e) - (\frac{k_1}{2.303})t$	$q_{e,cal}$ (mg/g)	17.5	15.7	16.9
	K_1 (min^{-1})	0.038	0.036	0.03
	R^2	0.9322	0.9788	0.8373
pseudo-Second-order kinetic $t/q_t = \frac{1}{k_2 q_e 2} + \left(\frac{1}{q_e}\right)t$	$q_{e,cal}$ (mg/g)	48.10	39.26	30.18
	K_2(g/mg min)	0.057	0.062	0.051
	R^2	0.9997	0.9998	0.9982
Elivich $q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} ln(t)$	α (g/mg min)	0.0263	0.0288	0.0414
	β (g/mg)	54.233	62.998	75.137
	R^2	0.8459	0.8422	0.8067

Conclusion

The polysulfone/ X% Fe_2O_3 mixed matrix membrane has been synthesized and used as an effective adsorbent for the removal of humic acids (HAs) from aqueous solutions. This investigation showed the applicability of polysulfone/ X% Fe_2O_3 mixed matrix membrane as a good, low-cost, and locally available adsorbent for the removal of humic acids (HAs) from aqueous solutions very good. The adsorption mechanism for these adsorbents was considered to be physical which was confirmed by the E_a obtained from Dubinin–Radushkevich isotherm. The kinetics studies concluded that humic acids (HAs) removal followed pseudo-second-order rate equation. Desorption studies indicated the good possibility of reusing the adsorbent. It is also suggested to investigate the applicability of this adsorbent for the removal of other material as well as its possible industrial application. The results obtained indicated the applicability of the present process for the efficient removal of pollutants from an aqueous solution.

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