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Enhanced removal of humic acids (HAs) from aqueous solutions using MWCNTs modified by N-(3-nitro-benzylidene)-N-trimethoxysilylpropyl-ethane-1,2-diamine on Equilibrium, thermodynamic and kinetics

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ABSTRACT

In this study, multi-walled carbon nanotubes modified by N-(3-nitro-benzylidene)-N-trimethoxysilylpropyl-ethane-1, 2-diamine (NBATSPED-MWCNTs) was prepared as a low-cost and non-toxic adsorbent. These materials was characterized by different techniques such as SEM, XRD and FT-IR and subsequently was used for the removal of humic acids (HAs) from aqueous solution. The influence of various operational parameters such as pH, initial (HAs) concentration and contact time in batch systems was investigated on the use of NBATSPED-MWCNTs. The kinetic results demonstrated that the pseudo-second- order equation is the best model to analyze the adsorption mechanism. The isotherm analysis showed that the equilibrium data are well fitted to the Langmuir isotherm model with maximum adsorption capacities of 12.5 mg g^{-1} of the adsorbent for removal of HAs. The overall adsorption process was exothermic and spontaneous in nature. The thermodynamic functions (ΔS^o, ΔH^o, ΔG^o) of the studied reaction are calculated using activated complex theory and show that adsorption (HAs) onto (NBATSPED-MWCNT) process requires heat.

Keywords: Humic acids; Isotherm; Kinetic; Thermodynamic; MWCNT.

1. INTRODUCTION

Different countries in the world often use chlorination to disinfect water and supply drinking water. The major concern regarding water disinfection with chlorine is the formation of potentially health-threatening disinfection by-products (DBPs). During chlorine disinfection, natural organicmaterial (NOM) reacts with chlorine to form DBPs [1,2]. Since 1974, numerous epidemiological studies have showed the correlation between the consumption of or contact with the chlorinated water and various cancers in humans and animals. Major chlorine disinfection by-products are trihalomethanes (THMs) and humic acids (HAs) which are toxic, carcinogenic, and mutagenic [3,4]. The presence of organic matters in water resources causes a lot of troubles during treatment processes especially the conventional water treatment. NOM are effective in different aspects of water treatment. The most important effect of these compounds is their reaction with chlorine and producing chlorination by products. It has been proved that chlorination by products depend on the concentration of NOM as the main precursor in the formation of these compounds. The conventional water

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treatment processes remove only 30% of NOM precursors [5,6]. Humic substances (mainly humic 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) [7]. Humic substances are complex high molecular weight organic compounds, with an aromaticaliphatic 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. 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 [8]. Humic substances are characterized by the presence of carboxylic acid and the hydroxy (phenol, alcohol), methoxy, and carbonyl groups. These groups and the aliphatic side chains are bound to the nucleus [9,10]. They are also recognized as potentially hazardous and carcinogenicsubstances [11], To prevent the formation of chlorinated hydrocarbons, it is necessary to reduce the content of humic substances in water or change the method of disinfection. The most common and economically feasible processes to reduce NOM are coagulation and flocculation followed by sedimentation/ flotation and filtration. Most of the NOM can be removed by coagulation, although hydrophilic, low molecular weight fractions of NOM (molecular mass up to 500) are apparently removed less efficiently (some fractions cannot be removed at all) than hydrophobic, high molecular weight compounds. Thus, low molecular weight fractions and hydrophilic NOM dominate the residual organic matter after coagulation. The best effect is achieved in the treatment of humic waters by clarification earlier in the acidic range (pH 4–6), which form large and wellseparated units [12]. However, as reported in the literature, using these methods poses many limitations such as the high operation cost and initial investment, obstruction, and generation of a large amount of sludge, reduction of water pH, production of corrosive water, and the need for reduction operation [13]. Conventional wastewater treatment protocol based on physicochemical, chemical, and biological processes includes coagulation and ion exchange [14], adsorption [15], ozonation and Air Oxidation [16], activated carbon filtration [17], and biosorption [18]. Among them, adsorption is widely used for large scale biochemical, chemical, environmental recovery, and purification applications [19]. This technique benefits from simple design and ease of operation by efficient non-toxic and low-cost adsorbents. Characteristics and appropriate selection of the adsorbent are based on factors such as removal capacity, treatment cost, and operating conditions [20]. Therefore, it is necessary to apply more appropriate methods for the removal of THMs and their precursors. Among different methods, the adsorption process is a simple and common method for the removal of organic pollutants like THMs and humic acid. In theory the activated carbon is a best adsorbent for THMs removal, however in practice it shows low capacity for the removal of high molecular organic compounds such as NOM [21].

For this reason, there is an urgent need to install innovative and cost-effective Technologies in the treatments cheme of THM stomeetstrict laws on for the removal of THMs from drinking water. Nanotechnology is the engineering of functional systems at the molecular scale, which offers new products and process alternatives for water purification, the advantage being that nanomaterials have a large surface- to-volume ratio [22].

Nevertheless, the effect of different experimental factors on the THMs removal by MWCNTs and modeling the responses of the adsorption capacities and THMs removal efficiencies have not been widely investigated except for a few examples [23,24]. Hence, the present study aims to contribute an understanding of the adsorption of THMs on MWCNTs by studying the influence of various experimental parameters on the adsorption process. Furthermore, various kinetics, isotherm models, and also nonlinear regression-based equations have been applied to describe the behavior of THMs-MWCWTs adsorption system. The structure of humic substances cannot be fully identified. Different, essentially hypothetical formulas are attributed; their task is to capture the particular positions of COOH and OH in a molecule, which significantly influences the properties of humic substances [25]. Among them, the wide application of adsorption is emerged from advantages including simplicity, low cost, high efficiency, wide adaptability and availability of different adsorbents [26]. The nature and properties of the adsorbent are of NBATSPED-MWCNT importance in this method. In practice, the main requirements for a solid sorbent are: (a) the fast and quantitative sorption and elution, (b) a high surface area and high capacity, and (c) high dispersibility in liquid samples [27]. In this work, the possibility of using NBATSPED-MWCNT as adsorbent for significant removal of HAS from aqueous solutions has been investigated. The effect of principle factors including pH, contact time between reagents, dosage of NBATSPED-MWCNT, initial HAS concentration was studied. The sorption equilibrium and kinetic data were analyzed by means of different models to understand the possible sorption mechanism of the HAS molecules onto the NBATSPED-MWCNTs.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

The chemical compounds and reagents used in this work were of analytical grade and purchased from Merck (Darmstadt, Germany). The structure of humic acids is shown in fig. 1. The standard and experimental solutions were obtained by diluting the stock solutions with deionized water. Deionized water (DI-water) obtained was used throughout this study [28].

2. 2. Preparation of NBATSPED-MWCNT

At first step, tri methoxy silylpro pylethylene diamine supported on MWCNT (NH2-MWCNT) was synthesized by the reaction of 1.8 mL N-(3-(tri methoxy silyl)-propyl) ethylene diamine and 10 mg MWCNT in 20 mL of dichloromethane under reflux at 40^{o}C in the oil bath for 24 hours. Then, the obtained solid was filtered, rinsed

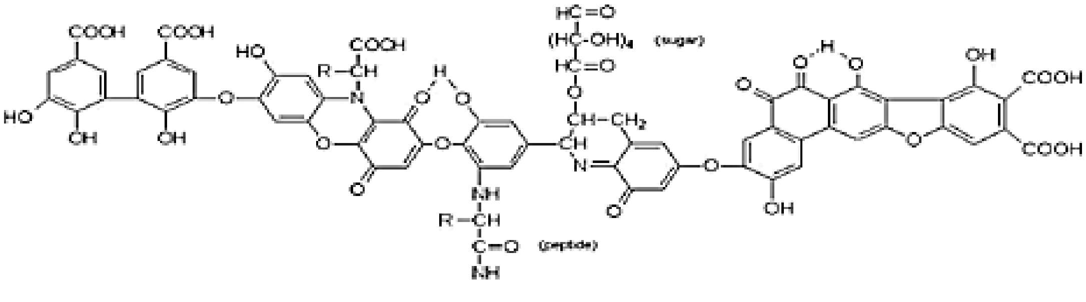

Fig. 1. Chemical structure of humic acid.

sequentially with ethanol and dried in an oven at 50°C. Then, 10 mg of 2 nitrobenzaldehyde was added to the resulting substance in 20 mL of methanol and refluxed at 60°C in oil bath for 24 hours. The product was filtered, washed with 50 mL of ethanol, distilled water and then dried in oven for 10 h 50°C. In this way, N-(3-nitro-benzylidene)-N-trimethoxysilylpropyl-ethane-1, 2-diamine supported on MWCNT (NBATSPED-MWCNT) was obtained as a new adsorbent.

2.3. Batch adsorption experiments

Batch adsorption experiments were carried out to determine the humic acids (HAs) adsorption isotherm onto NBATSPED-MWCNT composite and its thermodynamic properties: 500 mL solution having 100 mg/L concentration of humic acids (HAs) was 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 250 mL flasks containing fixed adsorbent dose of 20 mg/L. These flasks were agitated at a constant rate of 200 rpm in a temperature controlled orbital shaker maintained at 25^{oC} temperatures. One of the sample flasks was withdrawn from orbital shaker after fixed time intervals (5, 20, 30, 40, 50, 60, 70, 80 min) and analyzed for remaining metal ions present in the adsorbate solution. NBATSPED-MWCNT was separated from aqueous solution by filtration through Whatman No. 42 filter paper. The concentration of the humic acids (HAs) in solution samples were analyzed by using a "Shimadzu 6800 Atomic Absorption Spectrophotometer" equipped with an air-acetylene flame. The metal removal (%A) or removal efficiency of metal ion is evaluated by using the equation:

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

Where C_0 and C_e are the initial and final concentration of humic acids (HAs) in solution(mg/L), respectively. The amount (mg/g) of humic acids (HAs) adsorbed at equilibrium was calculated by using the following equation:

$$q_t=\frac{(C_o-C_t)\mathrm{v}}{w} \qquad (2)$$

where, C_o and C_t are initial ion concentration and concentration of humic acids (HAs) at any time't', while V is volume of solution in litters and w is adsorbent dosage in mg/L. To evaluate the thermodynamic properties of the adsorption process, 20 g of NBATSPED-MWCNT composite was added into 100 mL initial humic acids (HAs) concentration ranging from 2 to 25 ppm in each experiment. Each solution was shaken continuously for 12 min at 25°C.

After the solutions reached equilibrium, the humic acids (HAs) concentrations were measured and the desorption results were then obtained. Each experiment was carried out in triplicate and the average results are presented in this study.

3. RESULTS AND DISCUSSION

3.1. Apparatus and Characterization Methods

The IR spectrum of MWCNTs (Fig. 2), shows absorption peak at 1715 cm^1 corresponding to the stretching vibration of carbonyl groups. The broad peaks at 1180 cm^1 could be assigned to C–O stretching from phenolic, alcoholic, etheric groups and to C–C bonds. The new peak appearing at 3400 cm^1 corresponds to OH stretching. This peak can be assigned to the hydroxyl group of moisture, or carboxylic groups. The aromatic C-C stretch is observed at 1580 cm^{-1}in spectra of MWCNT before the functionalization [29].

The morphological features of the samples studied by SEM are shown in Fig. 3a and b. MWCNTs are observed to be smooth, homogeneous, tidy and approximately uniform in size distribution (Fig. 3a). After the surface modification with NBATSPED, the NBATSPED-functionalized MWCNTs became rough, larger and bundled (Fig. 3b)[30]. The XRD pattern of the NBATSPED-MWCNTs (Fig. 3c) represents a peak at 26.07^0 (002) corresponding to the interlayer spacing of the nanotube. The peaks at 43.34^0(100), 53.49^0 (004) and 78.5^0 (100) correspond to diffractions and reflections from the carbon atoms [31]. As seen, the highly crystalline nature of the MWCNTs after functionalizing with NBATSPED is confirmed, while the high intensity of peak at 53.49^0 (004) shows that there has been a small amount of material in amorphous state. The observed XRD pattern indicates that the prepared NBATSPEDMWCNT is well-synthesized.

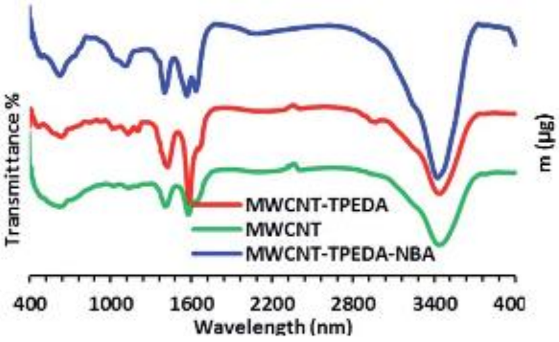

Fig. 2. FT-IR spectrum.

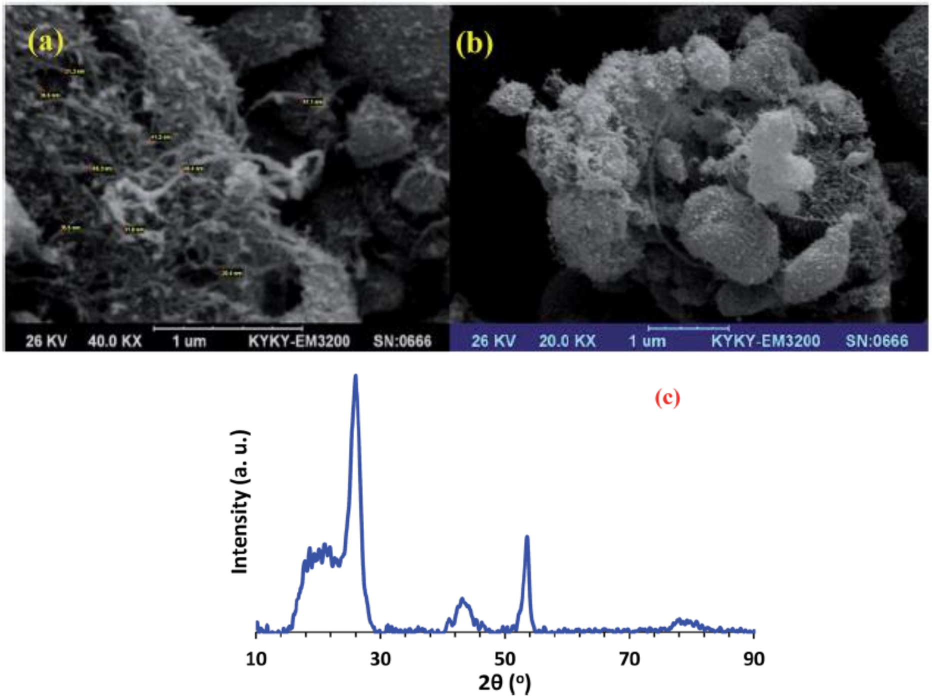

Fig. 3. SEM images of MWCNT (a), NBATSPED-MWCNT (b), and XRD pattern of NBATSPED-MWCNT (c).

3.2 Effect of pH

The pH has been identified as one of the most important parameter that is effective on humic acids (HAs) sorption. It is directly related with competition ability of hydrogen ions with humic acids (HAs) to active sites on the biosorbent surface. The effect of pH on the biosorption of humic acids (HAs) onto NBATSPED-MWCNT was studied at pH 2.0–8.0, Fig.3. The maximum biosorption was observed at pH 5.0 for humic acids (HAs). Therefore, the remaining all biosorption experiments were carried out at this pH value [32]. The biosorption mechanisms on the NBATSPED-MWCNT surface reflect the nature of the physic chemical interaction of the solution. At highly acidic pH, the overall surface charge on the active sites became. positive and humic acids (HAs) and protons compete for binding sites on NBATSPED-MWCNT, which results in lower uptake of humic acids (HAs). The biosorbent surface was more negatively charged as the pH solution increased from 5.0. The functional groups of the NBATSPED-MWCNT was more deprotonated and thus available for the humic acids (HAs). Decrease in biosorption yield at higher pH=5 is not only related to the formation of soluble hydroxylated complexes of the humic acids (HAs), but also to the ionized nature of the NBATSPED-MWCNT of the biosorbent under the studied pH. Previous studies also reported that the maximum biosorption efficiency of humic acids (HAs) on biomass was observed at pH 5.0.

3.3 Effect of NBATSPED-MWCNT amount

The amount of NBATSPED-MWCNT (adsorbent) was studied in the range of 0.2-2.5 g/L. Fig. 4 appears the effect of different amount of adsorbent on removal efficiency. The maximum removal of humic acids (HAs) was 94.6% at 1.75 g/L of adsorbents amount. The phenomenon of increase in percentage removal of humic acids (HAs) with increase in adsorbent dose may be explained as with increase in adsorbent dose, more and more surface becomes available for humic acids (HAs) to adsorb and this increase the rate of adsorption [33].

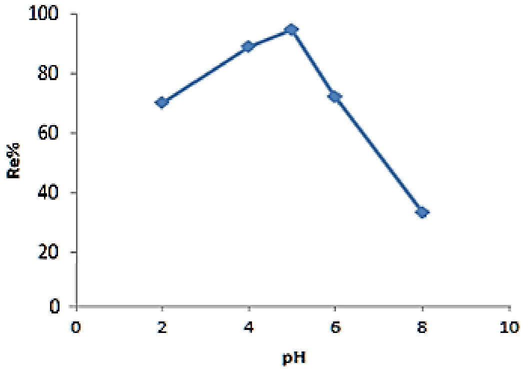

Fig. 4. Effect of pH on removal of humic acids (HAs) (conc. = 100 mg/L; adsorbent dose = 1.5 g/L; contact time = 60 min; stirring speed =200 rpm; temp = 25^{oC}).

3.4 Effect of contact time

It has been observed from Fig. 5. that rate of removal efficiency of humic acids (HAs) was increased from 42.52% to 94.6% with increased time from 30 to 180 min. Maximum removal was occurred at 120 min (equilibrium). It may be explained by the fact that initially for adsorption large number of vacant sites was available, which slowed down later because of exhaustion of remaining surface sites and repulsive force between solute molecule and bulk phase [34].

3.5 Effect of temperature

The effect of vary temperature (15, 25, 35, and 45^{oC}) and the thermodynamic parameters such as (ΔH^o), (ΔS^o), (ΔG^o) are necessary to estimate whether the reaction of adsorption is endothermic or exothermic. The thermodynamic parameters were calculated from Eqs. (4) and (5) [35-37]:

$$Ln\ K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (3)$$

$$\Delta G^0 = \Delta H^0 - \Delta S^0 T \qquad (4)$$

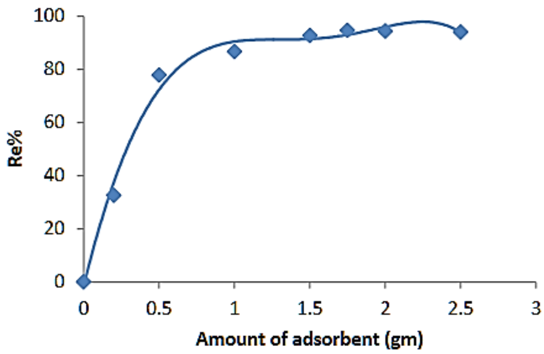

Fig. 5. Effect of NBATSPED-MWCNT amount on removal of humic acids (HAs) (conc. = 100 mg/L; pH= 5.0; contact time = 60 min; stirring speed =200 rpm; temp = 25^{oC}).

Where K_d is the distribution coefficient; ΔH(J/mol), ΔS(J/mol K), and T the enthalpy, entropy, and temperature in Kelvin, respectively; R is the gas constant (8.314 J/mol K) and Gibbs free energy change ΔG^0.

From the results in Fig.6 and Tables (1,2); it is showed that the adsorption is normally endothermic, thus capacity of adsorption for humic acids (HAs) increase at increase in temperature. The maximum rate of removal was reached at 45^{oC} which was 97.5%.

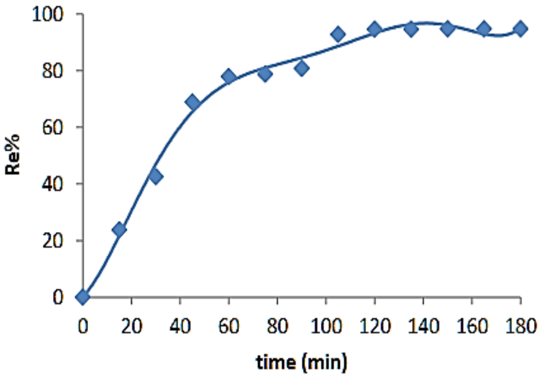

Fig. 6. Effect of contact time on removal of humic acids (HAs) (conc. = 100 mg/L; pH= 5.0; amount of NBATSPED-MWCNT = 1.75g/L; stirring speed =200 rpm; temp = 25oC).

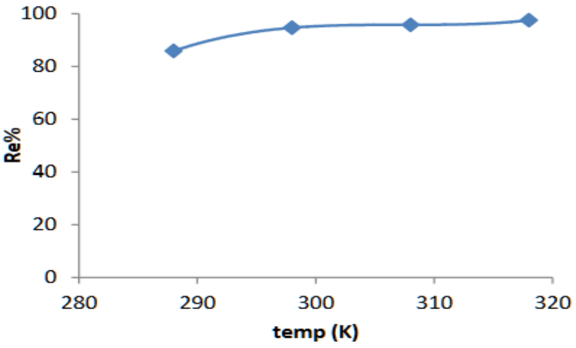

Fig. 7. Effect of temperature on removal of humic acids (HAs) (conc. = 100 mg/L; pH= 5.0; amount of NBATSPED-MWCNT = 1.75g/L; stirring speed =200 rpm).

Table 1. The distribution coefficients at different temperature

humic acids (HAs) concn. (mg/L)	R^2	K_d			
		288K	298K	308K	318K
100(mg/L)	0.936	6.07	17.86	22.8	39.0

Table 2. The thermodynamic parameters for the adsorption of humic acids (HAs) on sawdust adsorbent

humic acids (HAs) concn. (mg/L)	ΔH^o(kJ/mol)	ΔS^o(kJ/mol K)	ΔG^o(kJ/mol)			
			288K	298K	308K	318K
100(mg/L)	1.45	-31.6	9.11	9.42	9.75	10.05

The results indicated that the ΔG° values are positive and increased in their absolute values with temperature. This result suggested that a high temperature is favored for the adsorption of nickel ions on sawdust, displayed a spontaneous adsorption process.

The values of heat of adsorption, ΔH is positive for humic acids (HAs), showed that the adsorption process of humic acids (HAs) on NBATSPED-MWCNT was endothermic; negative ΔS suggested that the adsorption was enthalpy driven and spontaneous in nature.

3.6 Adsorption isotherms

Two models have been used in this study; namely Langmuir and Freundlich models. These isotherms represented the amount of solute adsorbed at equilibrium per unit weight of adsorbent, x/m (mg/g), to the adsorbate concentration at equilibrium, Ce (mg/L).

The Langmuir model represents one of the first theoretical treatments of nonlinear sorption and suggests that the uptake occurs on a homogenous surface by monolayer sorption without interaction between the adsorbed molecules. The linear form of the Langmuir adsorption isotherm is represented in Eq. (6) [38]:

$$\frac{C_e}{qe} = \frac{1}{bq_m} + \frac{C_e}{q_m} \qquad (5)$$

where: q_e is the sorbed metal ions on the biomass (mg/g), q_m is the maximum sorption capacity for monolayer coverage (mg/g), b is the constant related to the affinity of the binding site (L/mg), and Ce is metal ions concentration in the solution at equilibrium (mg/L) [39]. Constant for the adsorbate - adsorbent equilibrium and the capacity of monolayer b and q_e were identified from the slope and intercept of the Langmuir plot (Fig. 7). The Freundlich model can be applied for non-ideal sorption onto heterogeneous surfaces involving multilayer sorption. The linear Freundlich model isotherm was applied for the adsorption of humic acids (HAs) and is expressed as [40]:

$$Log\ q_e = Log\ k + \frac{1}{n} Log\ C_e \qquad (6)$$

where: K is the constant indicative of the relative adsorption capacity of the adsorbent (mg/g). 1/n is the constant indicative of the intensity of the adsorption. Both K and n being an indication of the extent of adsorption and the degree of non - linearity between solution and concentration, respectively [41].

The linear Freundlich plots are obtained by plotting log q_e versus log C_e from which the adsorption coefficients could be estimated (Fig. 8). All constants identified from Langmuir and Freundlich isotherms are given in Table 3. From above Table 4, it is clear that the best model used to estimate the removal process was Langmuir model according to the correlation coefficient (R^2).

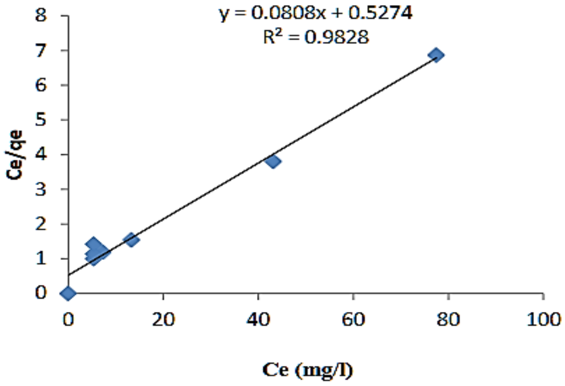

Fig. 8. Langmuir plot of humic acids (HAs) adsorption on NBATSPED-MWCNT (pH 5.0; rpm 200).

3.7 Kinetic adsorption models

The investigation of adsorption kinetics estimate the uptake rate of humic acids

(HAs), and obviously this rate controls the occupant time of these ions at the solid liquid interface. Hence it is imperative to evaluate the time dependency of such systems for different pollutant removal processes. Thus, the required contact time for the adsorption to be completed is essential to give knowledge into a sorption process. This also gives data on the base time required for impressive adsorption to happen and the possible diffusion control mechanism between the adsorbed ion as it moves from the bulk solution towards the adsorbent surface [42]. At the starting stage of the process of adsorption, the removal rate of i humic acids (HAs), is higher. The faster starting rate might be because of the acces sibility of the uncovered surface area of the adsorbent at first.

The adsorption kinetics relies upon; (i) the surface area of the adsorbent, (ii) the nature and concentration of the surface groups (active sites), which are in charge of interacting with targeted ions. The kinetics models include: the pseudo - first order and pseudo - second order [43]; Eq. (8) and (9); respectively.

$$\mathrm{Ln}(q_{eq}\text{-}q_t)=\mathrm{Ln}\ q_e - k_1 t \qquad (7)$$

$$\frac{t}{q_t}=\left(\frac{1}{k_2 q_{eq}^2}+\frac{t}{q_{eq}}\right) \qquad (8)$$

Where $q_{eq}$is the amount of metal sorbed at equilibrium (mg/g); q_t is the amount of metal sorbed at time t (mg/g); and k_1 is the rate constant of the first - order adsorption (1/min) and k_2 is the pseudo - second order rate constant (g/mg h). The slopes and intercept of ln (qe-qt) versus t plot (Fig. 9a) were used to describe the pseudo first order rate constants (k_1) and qe. A plot of t/qt versus t (Fig. 9b) was used to describe the pseudo - second - order rate [43,44].

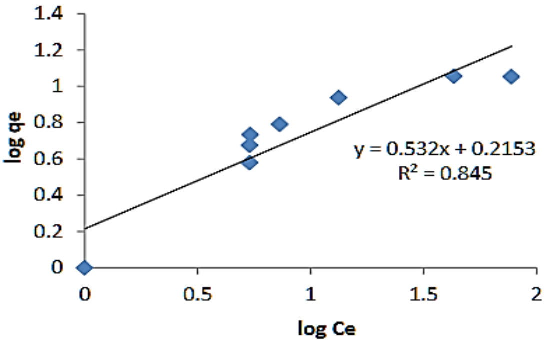

Fig. 9. Freundlich plot of humic acids (HAs) adsorption on NBATSPED-MWCNT t (pH 5.0; rpm 200).

Table 3. Parameters of the Langmuir, Freundlich isotherms for the adsorption of humic acids (HAs) onto NBATSPED-MWCNT

Parameters	Value humic acids (HAs)		
Langmuir Isotherm	q_{max} (mg/ g)	b (1/ mg)	R^2
	12.5	0.152	0.982
Freundich Isotherm	K (mg/ g) ((1/ mg)$^{1/n}$	1/n	R^2
	0.18	0.532	0.845

Table 4. pseudo - first - and - second - order kinetics for the adsorption of humic acids (HAs) onto NBATSPED-MWCNT

Kinetic Model	Pseudo first - order kinetic			seudo second-order kinetic		
	q_e(mg g^{-1})	k_1(1/min)	R^2	q_e(mg g^{-1})	k_2(g/mg min)	R^2
humic acids (HAs)	5.41	-0.02	0.527	5.62	10.91	0.942

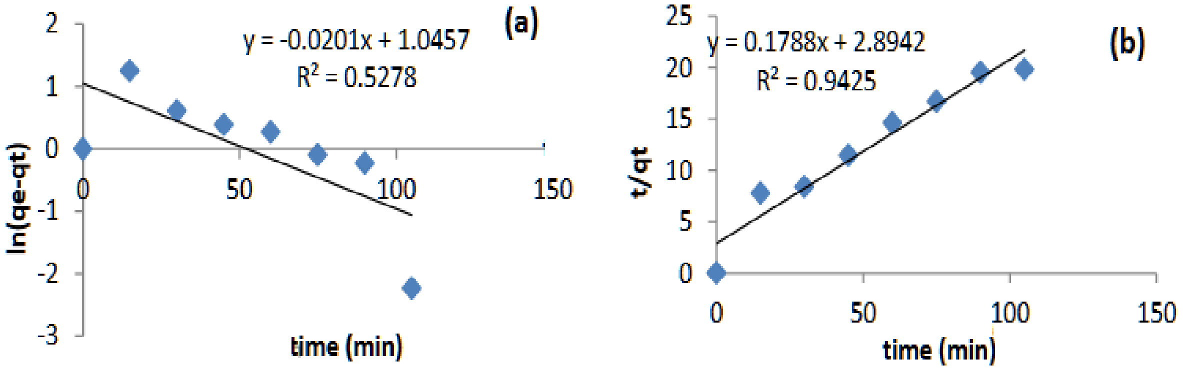

Fig. 10. kinetic models plot of humic acids (HAs) adsorption on NBATSPED-MWCNT: (a) pseudo - first - order model; (b) pseudo – second - order model.

The values of correlation coefficient (R^2) indicate a better fit of pseudo - Second - order model with the experimental data compared to pseudo - first - order model. The values of q_e calculated from the second order kinetic model compatibility well with the experimental values. Results showedin Table 4.

4. CONCLUSIONS

The N-(3-nitro-benzylidene)-N-trimethoxysilylpropyl-ethane-1,2-diamine on MWCNTs (NBATSPED-MWCNTs), has been synthesized and used as an effective adsorbent for the removal of humic acids (HAs) from aqueous solutions. The effects of adsorbent dosage, pH, contact time, and initial humic acids (HAs) on the removal of (HAs) was investigated through batch experiments. Isotherm models such as Langmuir and Freundlich for the adsorption process were evaluated and the equilibrium data were best described by the Langmuir model. The process kinetics was found to be successfully fitted to the pseudo-second-order kinetic model. Adsorption of (HAs) was found to be spontaneous at the temperatures under investigation. The positive value of ΔH° confirmed the sorption process was endothermic. The goal for this work is to develop inexpensive, highly available, effective humic acids (HAs) adsorbents from natural waste as alternative to existing commercial adsorbents[21,46-48]. (NBATSPED-MWCNT), has a high adsorption capacity when compared to other adsorbents for humic acids (HAs) removal from an aqueous medium.

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