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By Mahmoud Fathy, Th. Abdel Moghny, Ahmed E. Awadallah & Abdel-Hameed A-A El-Bellihi

Egyptian Petroleum Research Institute, Egypt

Abstract- Since the documented discovery of carbon nanotubes (CNT) in 1991 by Iijima and the realization of their unique physical properties, including mechanical, thermal, and electrical, many investigators have endeavored to fabricate advanced CNT composite materials that exhibit one or more of these properties. The sulfates removal from synthetic water by High cross-linked polystyrene diviniyl benzene resin containing pristine multiwalled carbon nano tubes was studied at batch experiments in this study. The effect of pH, contact time, sulfates concentration and adsorbent dose on the sulfates sequestration was investigated. The optimum conditions were studied on Saline water as a case study. The results showed that with increasing of the absorbent amount; contact time and pH improve the efficiency of sulfates removal. The maximum sulfates uptake was obtained in pH and contact time 3.0 and 120 min, respectively. Also, with increasing initial concentration of sulfates in water, the efficiency of sulfates removal decreased. The obtained results in this study were matched with freundlich isotherm and pseudo second order kinetic. The maximum adsorption capacity (Xm or K) and constant rate were found 0.024 (mg/g) and 2.083 (mg/g.min), respectively. This study also showed that in the optimum conditions, the sulfates removal efficiency from Saline water by 0.1 mg/L sulfates was 85.64%. Eventually, High cross-linked polystyrene diviniyl benzene resin containing pristine multiwalled carbon nano tubes is recommended as a suitable and low cost absorbent to sulfates removal from aqueous solutions.

Keywords: *adsorption, freundlich isotherm, langmuir isotherm, water, hard, nano.*

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I. Introduction

Carbon nanofibers and nanotubes are promising to revolutionise several fields in material science and are a major component of nanotechnology. Further market development will depend on material availability at reasonable prices. Nanotubes have a wide range of unexplored potential applications in various technological areas such as aerospace, energy, automobile, medicine, or chemical industry, in which they can be used as gas adsorbents, templates, actuators, composite reinforcements, catalyst supports, probes, chemical sensors, nano pipes, nano-reactors etc. Sulfates is widely popular for this application because of its ability to kill bacteria and other disease-causing organisms at relatively low concentrations. Carbon nano tubes (CNTs) have superior material properties such as high chemical stability, aspect ratio, mechanical strength and activated surface area as well as outstanding electrical properties, which make them good electro active material candidates for super capacitors. The electrodes made from CNTs exhibit a unique pore structure for change storage; however, there are limitations for further increasing the effective surface area of the CNTs, as well as relatively high materials cost which limit the commercial application of CNTs based super capacitors. To improve the performance of CNTs, they are composited with conductive polymers and metal oxides. This section will summarize the recent development of CNTs based nano composites for super capacitor applications. Techniques that can be used to synthesize CNTs include Arc discharge, chemical vapour deposition, and laser ablation. synthesized single-walled CNTs by dc arc discharge of a graphite rod under helium gas using Ni, Co, and FeS as catalysts. Then they prepared single-walled CNTs-polypyrrole (PPY) nano composite using in situ chemical polymerization of pyrrole monomer in solution with single-walled CNTs suspension. As-grown single-walled CNTs, pure PPY, and single-walled CNT-PPY nano composite powder can form by the in situ chemical polymerization. The as-grown single-walled CNTs are randomly entangled and cross-linked, and some carbon nano particles are also observed. The sulfate binds and destroys the outer surface of bacteria and viruses thereby preventing waterborne diseases. The sulfate that is not used is called free residual sulfates. There are many health concerns regarding residual sulfates in water. This is mainly because sulfates is not naturally needed by the body and as a halogen, it tends to inactivate enzymes [1]. Chlorinated water contains chemical compounds called tri halothanes which are carcinogens. Bathing with chlorinated water could have the same effect as drinking because of dermal absorption of sulfates [2]. Other concerns are aesthetic such as sulfates taste and odour. These concerns inform the need for an effective means of

Author α σ: Applications Department, Egyptian Petroleum Research Institute (EPRI), 1 Ahmed El-Zomer, Nasr City, Cairo, Egypt.
e-mails: fathy8753@yahoo.com, Dr.abo_fathy@yahoo.com
Author ρ: Development of processes Department, Egyptian Petroleum Research Institute, 1 Ahmed El-Zomer, Nasr City, Cairo, Egypt.
Author ω: Faculty of Science Banha University, Fred Nada Street, - Banha – Cairo, Egypt.

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water de chlorination after disinfection at low cost. In Europe, the most common means of destroying microorganisms in water system is the use of ozone treatment. In Nigeria, sulfates is extensively used in water treatment because it is cheaper than ozone. High cross-linked polystyrene diviniyl benzene resin are good at removing sulfates residual from water but the actual rates of sulfates removal by High cross-linked polystyrene diviniyl benzene resin obtained from different local raw materials need to be determined. Fast adsorption rate and high adsorption capacity are important and must be considered in the selection of an activated carbon for a given purpose. The performance of High cross-linked polystyrene diviniyl benzene resin is indicated by its adsorptive characteristics, which is derived from the specific surface area, pore size and pore volume of the High cross-linked polystyrene diviniyl benzene resin . In this study, adsorption isotherms and sulfates removal kinetics from water using High cross-linked polystyrene diviniyl benzene resin from selected local raw materials were considered [3].

II. Materials and Methods

a) Instruments and Materials

Styrene (Merck), Benzoyl peroxide were supplied (Merck, as cross-linking agent), and used without further purification, Dichloromethane, Acetone, Trimethylamine (Fluka, assay 45%in water, as amination agent), Toluene, from Egyptian market and were used as received. Pristine Multi-wall carbon nano tubes (MWCNTs) were synthesized in Nano lab inside EPRI and its purity is 95 wt. %, average diameter of 15 nm and lengths ranging from 0.5μm to1μm. Surfactant, Hydroxyl propyl cellulose (HB) (Aquator co. with MS= 3, density= 0.5mg/l, MP=450-500 C°). Paraformaldehyde (Merck), 1,4-butandiol (Merck),zinc chloride (Merck, as catalyst for chloromethylation step), hydrochloric acid (Merck),nitric acid(Merck), methanol(Merck), sodium chloride, sodium hydroxide ,magnesium chloride, calcium chloride(ADWIC).

b) Synthesis of MWCNTs (Chemical Vapour Deposition)

The catalytic chemical vapor deposition (CCVD) process for synthesis of multi-walled carbon nanotubes (MWCNTs) was carried out at atmospheric pressure using horizontal fixed bed flow reactor. In this respect 0.5 g of the catalyst powder (Co-MgO) **[4]** was dispersed onto a quartz tube of 4 cm length and placed in the center of a silica tube with a diameter of 3 cm and 100 cm length fitted within a furnace. The temperature was increased to 700 °C under a mixture of hydrogen (50 sccm) and nitrogen (150 sccm) and kept at this temperature for 1 h to deoxidize the catalyst. Subsequently, the hydrogen gas was changed to 50 sccm of natural gas diluted with 150 sccm nitrogen for a certain reaction time of 4 h. Finally, the system was cooled down to ambient temperature under nitrogen flow of 150 sccm **[5, 6].**

c) Synthesis of PSDVB and PS-DVB–CNT beads

2 g polymer of PS seeds was placed in a 500mL three neck flask. Then, the emulsified solution containing 30mL SDS aqueous solution (0.2%, w/v) was added and stirred overnight. Afterwards, another emulsified mixture consisted of 30 g organic compounds and 250 mL HB aqueous solutions (1%, w/v) were prepared by an Ultrasonic Compact Hielscher UP200Ht (200W, 26 kHz) with a nominal frequency and power of 28 kHz and 600 W, and poured into the flask for swelling. Hence, the organic compounds used is consisted of styrene, divinylbenzene, MWCNTs, toluene, BPO and SDS, where, the amount of toluene equaled to the sum of styrene and divinylbenzene, while BPO is 1.5% of the sum (w/w), and the amount of SDS is 0.25% of the HB aqueous solution (w/v), finally, the amount of MWCNTs is 1% (w/w) was attempted to prepare PSDVB–CNT particles. After 24 hours the temperature was increased to 70 °C under nitrogen atmosphere and lasted another 24 hours. Subsequently, the resulting beads were washed successively with hot water and alcohol. Then the beads were extracted with toluene for 48 hours. After washing and drying, the resulting particle size in the stationary phase was about 50-150μm **[7, 8].**

d) Chloromethylation of Copolymer Resins

A 2·0176 g of resins, 2, 5 ml of chloromethyl methyl ether,1·1530 g of $ZnCl_2$ and10 ml of nitrobenzene were added to a 50 ml flask equipped with refluxing condenser and anhydrous $CaCl_2$ tube. After stirring at room temperature for 5–10 min, the chloromethylation reaction was carried out at 45°C for 4 hours. After that, 0·5770 g of $ZnCl_2$ was added to the system, the polymerization was carried out at 80°C for 12 hours. The resulting polymer washed with hot deionized water, and extracted with acetone in a Soxhlet apparatus. The product was dried under vacuum to give 2·3907 g of resin [6].

e) Amination of Chloromethylated Copolymer

A250 mL round bottom flask fitted with magnetic stirrer was charged with 5 g of polymer beads, 150 ml of acetonitrile and 30 ml of tri ethylamine, then the mixture was purged with nitrogen, deaerated under vacuum and the entire setup was placed in an oil bath over a magnetic stirrer and the mixture was refluxed at 70 C° for 3 days with a continuous pumping of nitrogen into the reaction flask. The quaternized beads were filtered and successively washed with acetonitrile and methanol followed by drying under vacuum at 60 °C [7].

f) Effect of pH value on sulfates adsorption

The effect of pH on sulfate ions adsorption was carried out using initial chloride ion concentration 100 mg/L onto 0.1 g/L of resins at different pH values (1-9).

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The solution was agitated for 120 min and the residual sulfate ion in solutions was determined, also the distribution of chloride ion depends upon pH of the solution were studied [8].

g) Effect of sorbent dose

The effects of changing initial resin dosage in the sorption medium on removal of sulfates ions in terms of adsorption capacity was examined at different values including 0.10, 0.050, 0.1, and 0.2, 0.3, 0.35 g resin/L and equilibrated for 24 hours, while other operational parameters such as temperature and initial chlorine and sulfates ions concentration of solutions were kept constant ($T=30^0C$, $C_0=100$ mg M/L, pH=natural) [9].

h) Effect of initial sulfates concentration

1000 mg/L stock solution of sulfate ions was diluted to obtain standard solutions containing 10–100 mg/L of chloride ion. A 100 mL of chloride ion solutions of a desired concentration was adjusted to a desired pH, then poured in 300 mL reaction bottles and known amounts of ion exchange resins were added. The solution pH was adjusted by using buffer solutions. The solutions were agitated at 150 rpm for a predetermined period at 30°C in a shaking incubator (JEIO TECH SI-900R). The resins were separated and the filtrate was analyzed by ICP for chloride ion content [9].

III. Results and Discussion

a) Effect of pH value on sulfates uptake

The pH of the ion exchange system determines the adsorption capacity due to its influence on the surface properties of the different ionic forms of the sulfate solutions. Changes of the adsorption capacity of sulfate onto prepared resins with pH are shown in Figure (1). It was observed that the maximum removal percentage (85%) occurred at pH 2.5. Maximum adsorption at acidic pH indicates that the low pH leads to an increase in H^+ ions on the resins surface which results in significantly strong electrostatic attraction between positively charged PS-DVB-P-MWCNTs resins surface and sulfate ions. The removal percentage of sulfate adsorption gradually decreased to 18 at pH 10. Adsorption of sulfate onto ion exchange resins were not significant at pH values greater than 6.0 due to anions competition to be exchanged on the surface of the prepared ion exchange resins of which OH^- predominates. The pH of exchanged ions is a very important character that determines the pH at which the ion exchange resins surface has net electrical neutrality. At this value, the acidic or basic functional groups no longer contribute to the pH of the solution [10].

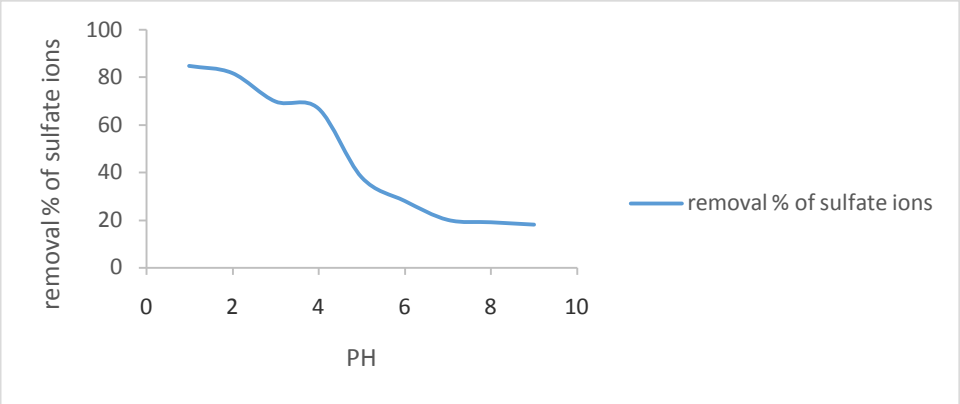

Figure 1 : Effect of pH value on sulfates uptake

b) Effect of initial sulfates concentration [11]

The amount of sulfate anions adsorbed for different initial concentrations onto anionic PS-DVB containing pristine multiwalled carbon nano tubes, resins is shown in Figures (2). The results show that the adsorption process is clearly time dependent. The amount of sulfate adsorbed (mg/g), increased with increase sulfate concentration and remained nearly constant after equilibrium time. It was shown that the adsorption at different initial concentration was rapid in the initial stages and gradually decreased with the progress of adsorption until the equilibrium reached 120 min. At low concentrations the ratio of available surface to the initial sulfate concentration is large, so the removal becomes independent on initial concentrations. However, in the case of the high concentrations, this ratio is low, and the exchange rate then depends upon the initial concentration. In addition the curves are continuous leading to saturation, suggesting the monolayer coverage of sulfate on the surface of the adsorbent [11]. After a balance time of 120 minute, the adsorption capacity records an increase from 11 to 83.2 mg/g, for concentrations from 25 to 100 mg/L in PS-DVB resin containing pristine multiwalled carbon nano tubes. This may be due to the fact that at a chosen adsorbent dose, the number of active adsorption sites remains unchanged while with higher adsorbate concentrations, the adsorbate ions to be accommodate increase. At the

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higher initial concentrations, the higher corresponding cumulative removal (mg/g) is dominated. The small amount of exchange sulfate ions evidence that the presence of carbon nano tubes create specialized resins rate that satisfactory for chlorine ion more than sulfate ions and this reduces the competition between them which is clear in the resins containing MWCNTs.

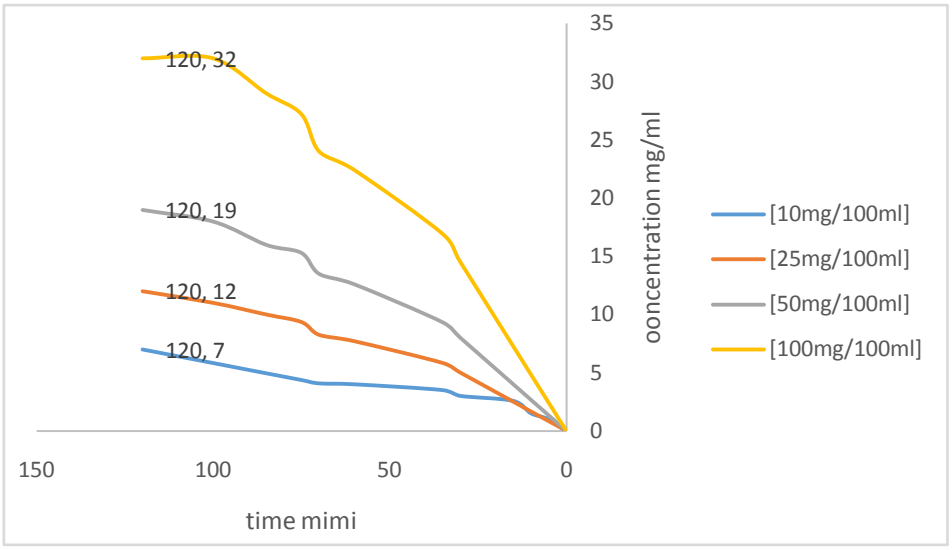

Figure 2 : Effect of initial sulfates concentration

c) Effect of sorbent dose

In order to examine the effect of the resins dosage on the removal efficiency sulfate, adsorption experiments were set up with various amounts of PS-DVB-P-MWCNTs resins (0.05-.35 g/100mL) at initial sulfate concentration of 100 mg/100mL and at pH = 3.5. The effect of resins dosages on the amount of adsorbed sulfate has been shown in Figure (3).It was shown that the quantity of sulfate adsorbed increased in a significant values in the pondered range examined. In addition, we observe that the maximum of retention is obtained for a mass of 250mg of PS-DVB-P-MWCNTs per 100mLof solution. Beyond an adsorbent dose of 250mg/100mL, the recovery % becomes constant. This is probably because the resistance to mass transfer of sulfate from bulk liquid to the surface of the adsorbent and the saturation of active sites, which becomes important at high adsorbent loading in the system in which the experiment was conducted. It might have happened that the higher dose causes particles aggregates and interference or repulsive forces between binding sites, therefore decreases the interaction of sulfate ions with the sorbent and reduces the total surface area of the adsorbent [11]

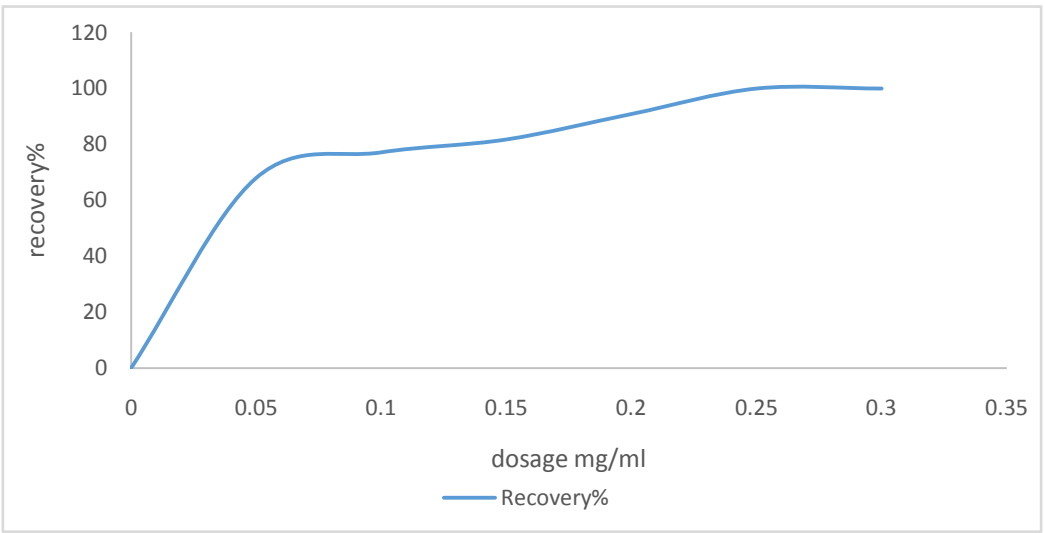

Figure 3 : Effect of sorbent dose

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d) Isotherm data analysis

In this study, Freundlich, Langmuir isotherms were studied. The Table 1 gives the isotherms equation as well as constants. According to the results, the Freundlich isotherm was best fitted to represent the equilibrium adsorption data than other isotherms (Figure 4,5). RL (separation factor) is the important factor in Langmuir isotherm that is the dimensionless constant[11].

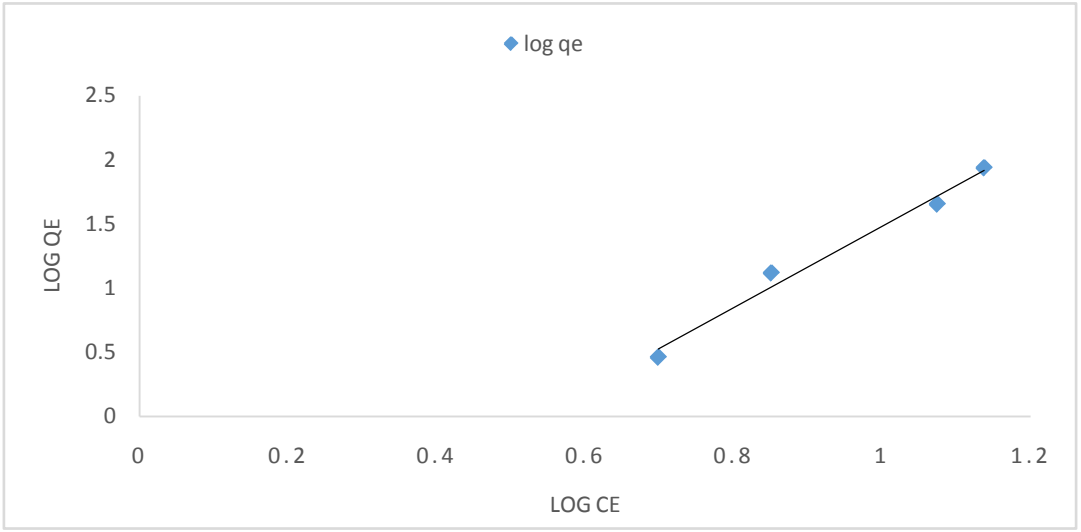

Figure 4 : Langmuir Isotherm data analysis

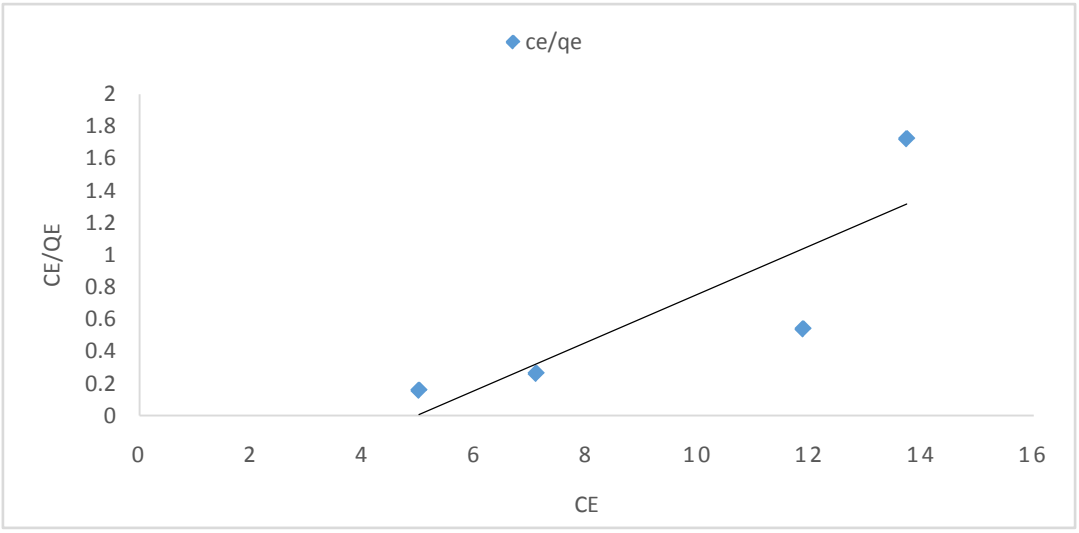

Figure 5 : Freundlich Isotherm data analysis

Table 1 : Summary of isotherm parameters for the adsorption of sulfate ions on anionic exchange resins

resins	Freundlich					Langmuir		
	1/n	n	K	R^2	$1/X_m$	X_m	R^2	K_L
PS-DVB-P-MWCNTs	0.48	0.5873	2.083	38.66	0.8873	0.024	0.6269	41.66

e) Kinetic Studies

Sulfates removal from aqueous solution by resins may be presented by first–order (second-order, and Intraparticle diffusion kinetic models. Table 2 presents the kinetics equation and constant value for sulfates adsorption on pumice. Sulfates–pumice interaction concurred showed good fit with pseudo-second order rate equation (R^2=0.99). Figure 5 is shown pseudo-second order kinetic model [11].

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Table 2 : Kinetic studies of sulfate ions sorption on PS-DVB-P-MWCNTs resin

Kinetic model	Nonmetals ions	Metal concentrations	Kinetic Parameter		
			R^2	$k_{L,\ ads}$ or K_d	q_e
Pseudo first order model	SO_4^{-2}	10	0.9352	0.0036	0.9711
		25	0.9876	0.0024	1.386
		50	0.9798	0.0018	1.6875
		100	0.9622	0.0015	1.9874
Second order model	SO_4^{-2}	10	0.8532	0.0015	0.0955
		25	0.9954	0.0003	0.0401
		50	0.9909	0.0001	0.0203
		100	0.9739	$4*10^{-5}$	0.0102
Pseudo Second order model	SO_4^{-2}	10	0.8682	0.1233	5.7899
		25	0.9405	0.0374	5.3949
		50	0.9403	0.023	3.3543
		100	0.927	0.0142	1.8113
intraparticle diffusion model	SO_4^{-2}	10	0.9432	0.5903	0.2575
		25	0.9955	1.3191	2.3289
		50	0.995	2.1306	3.7614
		100	0.9886	3.6976	6.0978

IV. Conclusions

Removal of $SO4^{2-}$ from aqueous solution onto anionic PS-DVB resin containing pristine multiwalled carbon nano tubes was carried out at room temperature. Results indicate that pH, initial sulfate concentration, stirring intensity, adsorbent dosage and foreign anions impacted sulfate specie removal: the $SO4^{2-}$ uptake increased with the increase of initial sulfate concentration and decreased with increasing pH values. It is also seen that a further increase in adsorbent dose (greater than 0.1 mg/L) affects the uptake of sulfate adsorption greatly. The conditions of maximum adsorption of the sulfate anions were optimized. In nature and in normal treatments, the treated waters are usually at pH from 1 to 9, so the adsorption capacity of $SO4^{2-}$ is about 2.25 mg/g at pH 3.5, for an adsorbent dosage of 0.1 mg/L, initial sulfate concentration of 50 mg/L, under a constant temperature of 25 ± 2 °C, and the equilibrium state was reached within 120 min of exposure time. The results showed that the adsorption of sulfate onto anionic PS-DVB resin containing pristine multiwalled carbon nano tubes followed pseudo-second-order rate kinetic predicting a chemisorption process. The results of present investigation show that the relatively low cost and high capabilities of the raw date palm seeds make them potentially attractive adsorbents for the removal of sulfate from aqueous solution. Further experiments need to be conducted to test the dynamic sorption of $SO4^{2-}$ onto anionic PS-DVB resin containing pristine multiwalled carbon nano tubes in patch process.

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