

Removal of Manganese from Petrochemical Effluent using Black

Carbon: Isotherm and Kinetic Studies

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Abstract

Black carbon from rice straw was introduced as adsorbent to remove Mn (II) from synthetic and petrochemical effluents and chemically modified using a mixture of H₂SO₄-HNO₃ to improve its adsorption properties. Batch adsorption studies were also optimised, considering at factors such as pH, amount of adsorbent, contact time and agitation speed. Optimum conditions were used for modeling studies. Adsorption properties were further studied by determining Freundlich, Temkin and D-R isotherms. In our study, the obtained experimental data best fitted with the D-R isotherm. Further, the kinetics of adsorption interactions were evaluated with three models for pseudo-first order, pseudo-second order and intra-particle diffusion respectively. The results demonstrated a best fit with pseudo-second order kinetics. In optimum conditions obtained during this research, were applied to petrochemical effluent, and up to 95% of Mn (II) could be removed using modified rice straw - black carbon.

Keywords: adsorption, modification, optimization, kinetic, isotherm

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1. Introduction

Heavy metals adversely affect the environment and high amounts can be toxic for living beings. They released into the environment have been increasing continuously as a result of industrial activities and technological development, posing a significant threat to the environment and public health because of their toxicity, accumulation in the food chain and persistence nature [1,2]. Exposure to heavy metal contamination has been found to cause kidney damage, liver damage, and anemia in low doses, and in high concentrations, heavy metals can be carcinogenic [3]. Mn (II) is used as catalyst for production of crude terephthalic acid (CTA) in petrochemical industry [1]. Therefore, Mn (II) in effluents produced by this industry is a major contaminant. The maximum acceptable level for Mn (II), set by the United States Environmental Protection Agency (USEPA) in the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) is 0.05 mg/L [4]. Mn (II) affects the nervous system resulting in Parkinson-like diseases which disturb the control of movement activities [5]. Different methods like chemical precipitation, ion exchange, electro dialysis and reverse osmosis [6-9] have been used for heavy metals removal. These methods tend to be expensive and time consuming. Adsorption is a new method for heavy metal removal which has been reported in several studies [10, 11]. This process depends on parameters such as adsorbent properties, initial concentration of adsorbate, amount of adsorbent, contact time and pH [12].

The application of activated carbon as an adsorbent for treatment of industrial effluents is not

sufficiently efficient and economically feasible. During the recent years, the biosorbents and inexpensive materials such as sawdust, rice wastes, tree bark and natural soils [13-16] have been used for removal of heavy metals. The incomplete combustion of rice straw (RS) results in black carbon (BC) which is a contaminant of agricultural soils [17]. However, BC has demonstrated a high adsorption capacity and may thus be used as adsorbent in effluent treatment. Chemical modifications have been shown to improve the adsorptive properties of adsorbents [18]. Thus, chemical modification increases sorption capacity of the BC.

The aim of this study is to assess the ability of non-modified and modified BC produced from RS to remove Mn (II) from synthetic and petrochemical effluents. Quality of adsorption was analysed using three isotherms: Freundlich, Temkin and D-R, in an effort to determine the best model to design a batch adsorption unit and Optimum conditions were successfully applied to a batch of real petrochemical effluent.

2. Experimental

2.1. Materials

Mn (NO₃)₂.4H₂O used for production of Mn (II) containing solution was purchased from Merck. To adjust pH, H₂SO₄ (0.01M) and NaOH (0.1M) were used. For chemical modification of adsorbent, concentrated H₂SO₄ and HNO₃ were used. All solutions used in this study were made using doubly distilled water (DDW).

2.2. Adsorbent

To prepare the adsorbent, RS samples were collected from agricultural lands of Rayjankari village (Mamasani County, Fars province, Iran). The RS was dried and burned in free air. The produced BC was collected and kept in polyethylene vessels. In order to homogenize BC ingredients, they were sifted through a sieve (mesh 80) (ASTM) and then BC washed with DDW to remove soluble salts. The residue was dried for 12 h in oven at 100 °C. Finally, the produced BC was applied for experiments as non-modified RS-BC (NMRBC). Some NMRBC was modified to improve its

sorption capacity. For this goal, it was suspended in a 3:1 mixture of conc. H_2SO_4 and conc. HNO_3 . The suspension was agitated for 8 h on a shaker (400 rpm). Then, the mixture was filtered and washed with DDW to remove any remaining acid. Finally, the residue was dried for 8 h at 85 °C in an oven and then used as modified RS-BC (MRSBC) for adsorption tests.

2.3. Adsorbent Analysis

The FT-IR spectra for both NMRSBC and MRSBC adsorbents were recorded in KBr 1% (IR-grade, Wako). The FT-IR spectrum was recorded in transmission mode using Valor III (JASCO) spectrophotometer with a MCT detector with resolution of 1 cm^{-1} .

2.4. Batch system experiments

The concentration and volume of Mn (II) in all experiments were 50 mg/L and 60 mL, respectively. The pH effect on Mn (II) adsorption in synthetic effluent was determined in the pH range of 2.8 to 9.6. The amount of adsorbent was 0.2 g. Each solution was agitated for 60 min at 500 rpm. To study the effect of adsorbent amount on adsorption of Mn (II), the amounts of adsorbents were varied from 0.1 to 1.6 g. In this stage, pH of each solution was adjusted at 6.5 and each solution agitated for 60 min at 500 rpm.

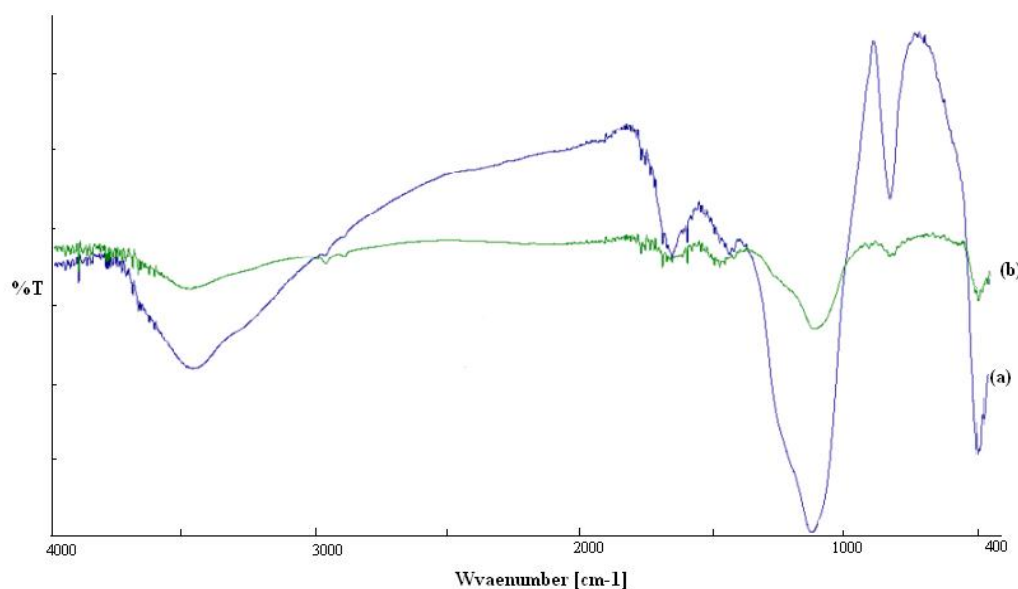
The effect on adsorption of contact times ranging from 30 to 240 min was studied. The pH was kept at 6.5, the amount of adsorbent was 0.5 g and each solution was agitated at 500 rpm using shaker apparatus. In order to investigate the effect of the agitation speed on the Mn (II) removal from solution using the adsorbents, the agitation speeds were varied from 200 to 800 rpm, and 0.5 g of adsorbent was used. The pH of each solution was 6.5 and agitation lasted 60 min. The experiments related to adsorption isotherm were studied at 19 ± 1 °C for various concentrations ranging 20 to 80 mg/L at pH 6.5. The amount of adsorbent was 0.5 g. Each solution was agitated for 60 min at 500 rpm.

3. Results and discussion

3.1. Adsorbent characteristics

Figure 1 shows FT-IR spectrum for the NMRSBC and MRSBC adsorbents. The absorption band at 3424 cm^{-1} in both adsorbents characterizes the stretching bond of hydroxyl group of phenolics [19]. Weak bands at 1438 cm^{-1} show the changing mode of surface deformation of hydroxyl group [20]. The band at 1619 cm^{-1} shows the stretching contribution of C=O in aromatic cycle of both acid and base groups [21]. Two bands at 1090 and 797 cm^{-1} also demonstrate the C₆O stretching bonds and aliphatic deformation of CH₂, respectively [22]. Both bands are stronger for MRSBC adsorbent than NMRSBC. Therefore, the adsorption capacity of MRSBC is higher compared with the NMRSBC.

Fig 1; FT-IR spectra of the adsorbent samples: (a) MRSBC, (b) NMRSBC

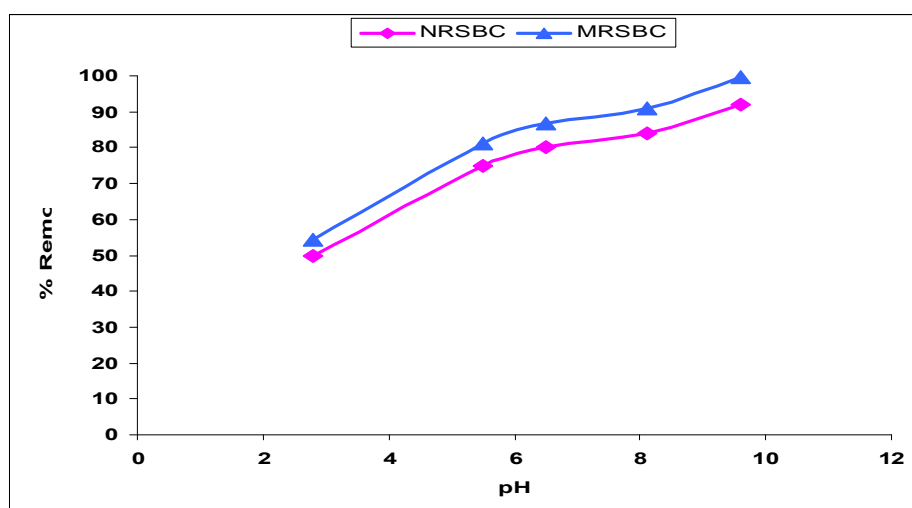


3.2. pH effect

Figure 2 demonstrates the pH effect on the percentage of Mn (II) removal by either NMRSBC or MRSBC. At pH range 2.8 to 6.5, the percentage of Mn (II) removal using either adsorbent rapidly increased whereas at pH ranging 6.5 to 8.1, it only increases slightly. At pHs over 8.1, the percentage of Mn (II) removal rapidly increased again. As can be seen in figure 2, MRSBC removes almost 10% more Mn (II) than NRBSC. The decrease of removal at low pH may be due to competition of H⁺ ions with Mn (II) ions for occupation the active sites on the surface of adsorbent. With increasing pH, the

concentration of H^+ ions decreases. Therefore, the percentage of Mn (II) removed with increasing pH, also increases. The adsorption edge is a range of pH (usually 2 units wide) where the efficiency of species removal reaches from a very low level to a maximum value [23]. Figure 2 shows that the adsorption edge for both adsorbents NMRSBC and MRSBC is at critical range from 3 to 5. Considering that metal ions precipitate as hydroxides at high pH, the optimum pH for Mn (II) adsorption by NMRSBC and MRSBC is 6.5.

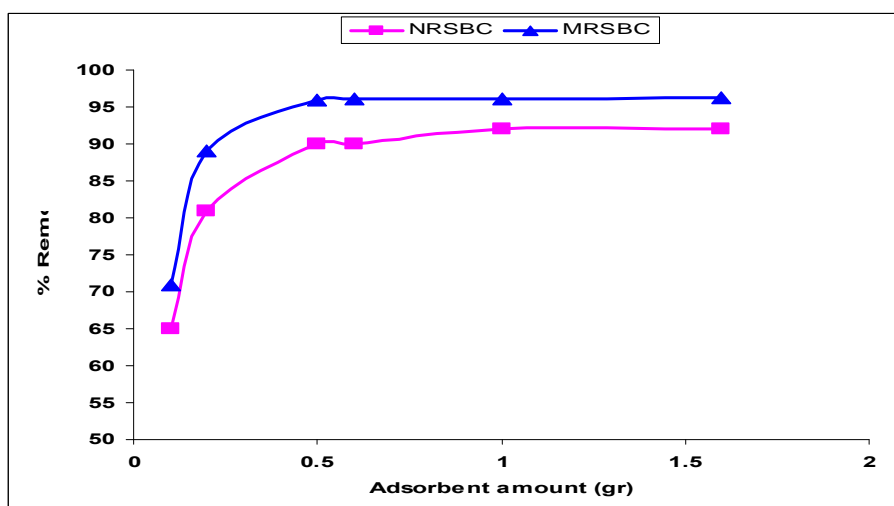
Figure 2; The effect of pH on the removal percentage of Mn (II) using NMRSBC and MRSBC



3.3. The effect of adsorbent amount

The effect of adsorbent amount for NMRSBC and MRSBC on Mn (II) removal is shown in Figure 3. When increasing the amount of adsorbent from 0.1 to 0.5 g/60 mL, the percentage of Mn (II) removal increases, but a further increase in the amounts of each of the adsorbents did not result in a further increase of the removal percentage. The increase of percent of Mn (II) removal with increase of the adsorbent amount can be explained by the increase in surface area and active sites [24].

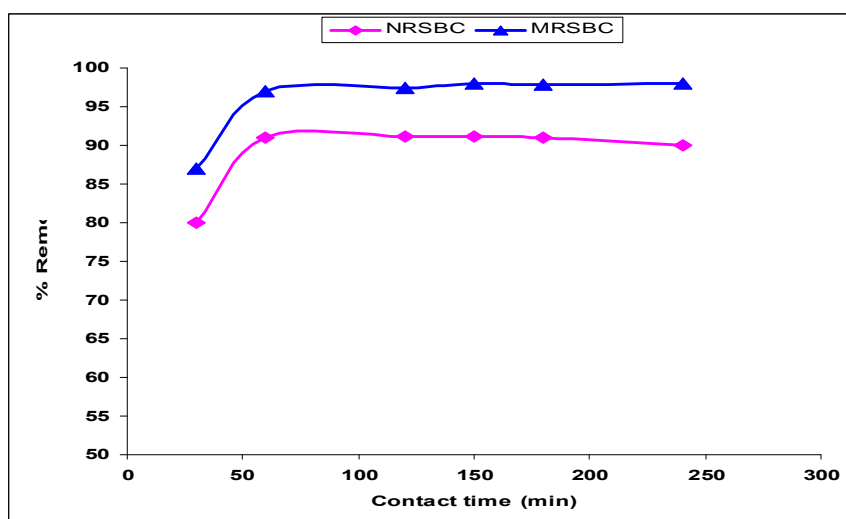
Figure 3; The effect of amount of NMRSBC and MRSBC adsorbents on the removal percentage of Mn (II)



3.4. The effect of contact time

The effect of contact time on the removal of Mn (II) for NMRBC and MRSBC is shown in Figure 4. With contact times ranging 30 to 60 min, the percentage of removal steadily increases, but after that time no further removal was detected. Thus, at time 60 min, the percentage removal reaches its maximum value and further increasing the contact time does not further affect removal percentage. Therefore, the time 60 min is the optimum contact time between adsorbents and Mn (II).

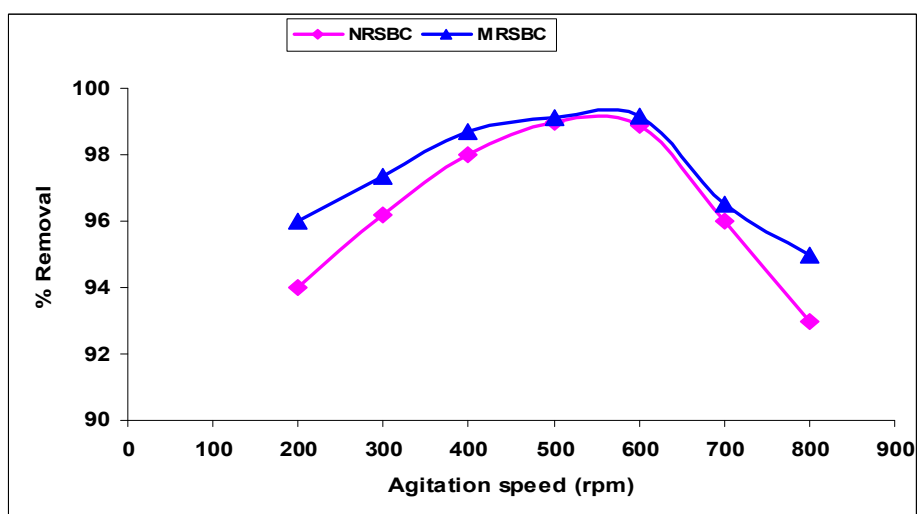
Figure 4; Influence of contact time of NMRBC and MRSBC adsorbents on the removal percentage of Mn (II)



3.5. The effect of agitation speed

The effect of agitation speed on adsorption of Mn (II) is shown in Figure 5. From 200 to 500 rpm, the percentage removal increases but after that it descends. The increase of the percent of removal with increasing agitation speed is due to the increase of mass transfer of Mn (II) from solution to surface of adsorbent. The decrease in removal of Mn (II) at higher agitation speeds may be due to desorption starting to occur [25].

Figure 5; The effect of agitation speed on the Mn (II) removal efficiency using NMRsBC and MRSBC adsorbents



The obtained optimum conditions, is presented in Table 1 for Mn (II) adsorption using NMRsBC and MRSBC.

Table 1. Optimum conditions for the removal of Mn (II) using NMRsBC and MRSBC adsorbents

<i>Parameter</i>	<i>Studied range</i>	<i>Optimum</i>
pH	2.8-9.6	6.5

Adsorbent amount(gr)	0.1-1.6	0.5
Contact time(min)	30-240	60
Agitation speed(rpm)	200-800	500

3.6. Adsorption isotherm

Adsorption is usually described through isotherms. In this study, three isotherms i.e. Freundlich, Temkin and D-R were determined for adsorption analysis of Mn (II) on NMRSBC and MRSBC.

The Freundlich isotherm explains the adsorption of heterogeneous surfaces and the multi layers adsorption of adsorbate on adsorbent [26]. The logarithmic form of isotherm is as following:

$$\text{Log} q_e = \text{Log} K_F + \frac{1}{n} \text{Log} C_e \quad (1)$$

Where q_e (mg/g) is amount of adsorbed material per mass unit of adsorbent in equilibrium state, C_e (mg/L) is concentration of adsorbate in equilibrium state, K_F ((mg/g) (L/mg)^{1/n}) is the constant related to the adsorption capacity and n , is the intensity of adsorption. The amounts of n and K_F can be calculated using the plot of $\text{Log } q_e$ versus $\text{Log } C_e$ and determination the slop and intercept.

The Temkin isotherm is based on the assumption that the fall in the heat of adsorption is linear [27]. In this isotherm, the adsorption occurs on heterogeneous surfaces and the effect of adsorbate interactions is considered [28]. General form of the isotherm is expressed as:

$$q_e = \frac{RT}{b} \text{Ln}(a C_e) \quad (2)$$

Where R (J/K.mol) is the gas constant, T (K) is absolute temperature, b (J/mol) is the constant related to the adsorption temperature and a (L/mg) is the constant for the Temkin isotherm. Equation (2) is can also be expressed as:

$$q_e = B \text{Ln} a + B \text{Ln} C_e \quad (3)$$

Where $B=RT/b$. the amounts of a and b can be obtained from slope and intercept of plot q_e

versus $\ln C_e$.

The D-R isotherm expresses that adsorption process is along with ion exchange [29]. The linear form of this isotherm is as following [30]:

$$\ln q_e = \ln q_m - K\varepsilon^2 \quad (4)$$

Where q_m (mol/g) is maximum of adsorption capacity and $K ((\text{mol})^{-2} / (\text{KT})^{-2})$ is the constant related to adsorption.

Polanyi potential (kJ/mol) can be calculated as following:

$$\varepsilon = RT \ln(1 + (\frac{1}{C_e})) \quad (5)$$

Where the unit of C_e is mol/L. the amounts of q_m and K can be calculated from slope and intercept using the plot of $\ln q_e$ versus ε^2 . Moreover, the isotherm D-R could explain the mechanism of adsorption using mean free energy (E) which is computable through following equation:

$$E = \frac{-1}{\sqrt{2K}} \quad (6)$$

If $|E|$ is between 8 and 16 kJ /mol, the adsorption process is basically a surface adsorption along with ion exchange but for $|E|$ ranging from 1.0 to 8.0 kJ /mol, the process needs to be explained via a physical mechanism [31].

The constants of aforementioned three isotherms for experimental data are given at Table 2 and Figures 6 - 8 show the plots of these isotherms. Regarding the correlation coefficients, experimental data show more adaption with D-R isotherm when compared with two other isotherms for both adsorbents.

Table2. Adsorption isotherm constants and correlation coefficients for the adsorption of Mn (II) on NMRSBC and MRSBC adsorbents at 19 ± 1 C°

Adsorbent	Freundlich isotherm constants	Temkin isotherm constants	D-R isotherm constants
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	K_F	n	R^2	a	b	R^2	q_m	K	E	R^2
NMRSBC	1.426	0.89	0.8850	0.857	422.78	0.9763	0.926	0.0087	7.6	0.9998
MRSBC	1.998	0.99	0.9172	1.143	458.90	0.9827	1.092	0.0077	8.1	0.9989

$K_F ((\text{mg/g}) (\text{lit/mg})^{\frac{1}{n}})$ and n = Freundlich constants

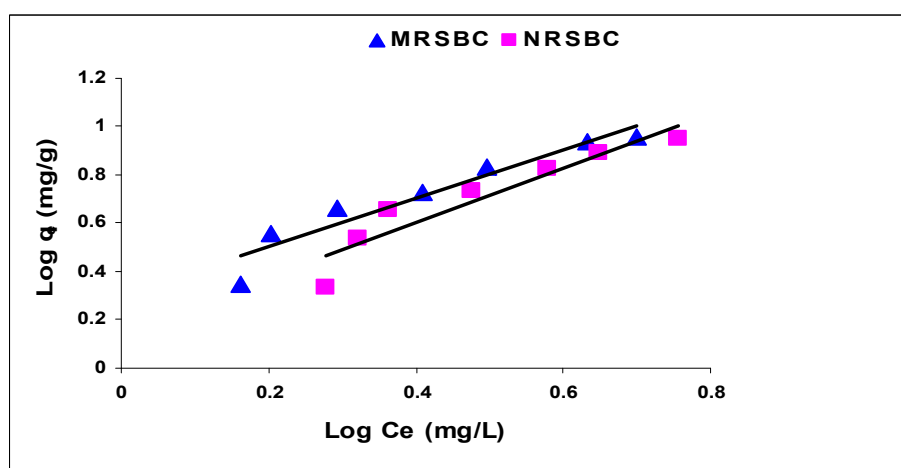
a (L/mg) and b (J/mol) = Temkin constants

q_m (mol/g) = maximum of adsorption capacity

K (mol^2/kJ^2) = D-R isotherm constant

|E| (kJ/mol) = mean free energy

Figure 6; Freundlich isotherm plot for the adsorption of Mn (II) using NMRSBC and MRSBC adsorbents



According Table 2, the amount of q_m for MRSBC adsorbent (1.092 g/mol) is higher than the amount of q_m for NMRSBC adsorbent (0.926 g/mol). This comparison shows the improvement of the adsorbent capacity for adsorption using chemical modification.

Figure 7; Temkin isotherm plot for the adsorption of Mn (II) using NMRSBC and MRSBC adsorbents

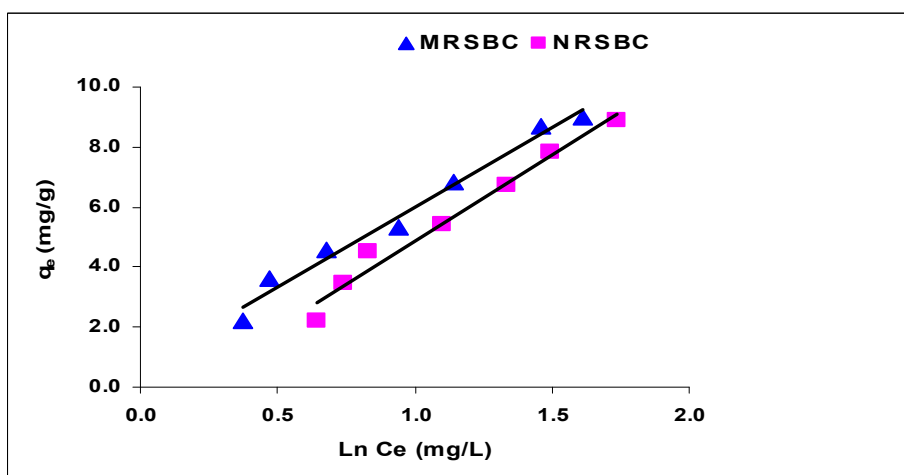
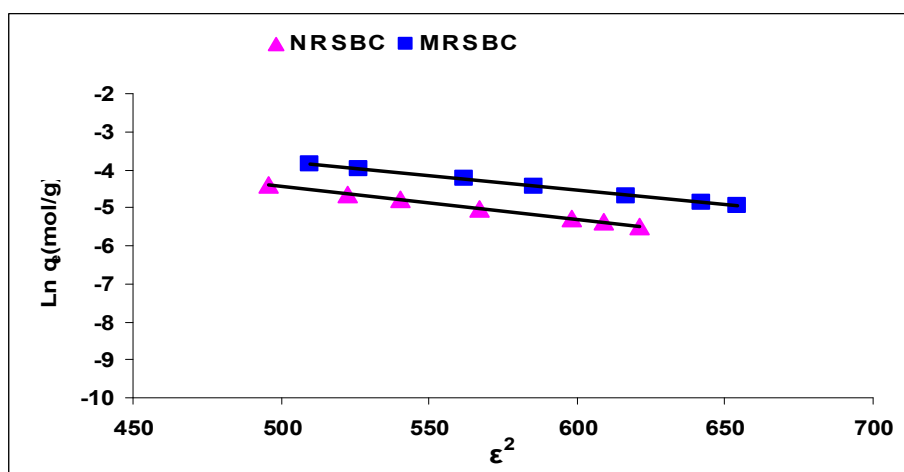


Figure 8; D-R isotherm plot for the adsorption of Mn (II) using NMRsBC and MRSBC adsorbents



The amount of n in Freundlich isotherm for MRSBC adsorbent is further than NMRsBC adsorbent and this demonstrates the higher efficiency of Mn (II) adsorption on MRSBC than NMRsBC. The amount of calculated $|E|$ for MRSBC is between ion exchange amounts whereas; the amount of calculated $|E|$ for NMRsBC is between the amounts of physical adsorption mechanism.

3.7. Adsorption kinetics modeling

The kinetics of adsorption as removal rate of adsorbate controls the residence time of adsorbate between solid and solution. Kinetic studies of adsorption are necessary for determination of adsorption efficiency and identification the type of adsorption mechanism. There are different models to investigate adsorption kinetics. In this study, the pseudo-first order, pseudo-second order and intra-particle diffusion models were investigated. The kinetic expression of pseudo-first order equation is as following [32]:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad (7)$$

Where, q_t (mg/g) is the adsorption capacity at time t , q_e (mg/g) is the adsorption capacity at equilibrium time and K_1 (1/min) is the rate constant for pseudo-first order adsorption. Integration of equation (7) and applying the boundary conditions $q=0$ to $q=q_t$ at $t=0$ to $t=t$ leads to make equation (8):

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (8)$$

The amounts of q_e and K_1 can be calculated using plot $\ln(q_e - q_t)$ versus t .

The mathematical conception of pseudo-second order equation of adsorption is as following [33]:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (9)$$

Where, K_2 (g/mg.min) is the rate constant for pseudo-second order adsorption. Integration of equation (9) and applying the boundary conditions $q=0$ to $q=q_t$ at $t=0$ to $t=t$ causes to make equation (10):

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + K_2 t \quad (10)$$

The equation (10) can be rearranged as equation (11):

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \quad (11)$$

In equation (11), the amount of $K_2 q_e^2$ is defined as initial adsorption rate and expressed as h (mg/g.min) [34]. The amounts of K_2 and q_e can be determined using plot t/q_t versus t in equation (11).

The process of adsorption is classified in two stages: as transfer of adsorbate molecules from aqueous phase to adsorbent surface and their diffusion into porous of the adsorbent. In intra-particle diffusion kinetics, the second step is slow and therefore is the rate determining step (RDS) [35]. The expression of this kinetic is as equation (12):

$$q_t = K_i t^{\frac{1}{2}} \quad (12)$$

Where, K_i ($\text{mg/g.min}^{1/2}$) is the rate constant of intra-particle diffusion kinetic. The constant K_i can be calculated via plot q_t versus $t^{1/2}$. If the plot is linear (regarding the amount of correlation coefficient) and also intercept is zero, the mechanism of adsorption will be intra-particle diffusion, and then second step is RDS.

The constants related to three pseudo-first order, pseudo-second order and intra-particle diffusion models for experimental data are given in Table 3 and Figures 9 - 11 show the plots of these models at time 60 min (optimum time) and a Mn (II) concentration of 50 mg/L.

Table 3. Different kinetic parameters for the adsorption of Mn (II) on NMRSBC and MRSBC adsorbents

Adsorbent	$q_e(\text{exp})$	Pseudo-first order			Pseudo-second order				Intra-particle diffusion		
		K_1	$q_e(\text{theor})$	R^2	K_2	$q_e(\text{theor})$	h	R^2	K_i	b	R^2
NMRSBC	5.712	0.0605	1.48	0.9650	0.046	6.02	1.67	0.9998	0.4310	2.8580	0.9097
MRSBC	6.300	0.0459	2.79	0.9695	0.032	6.67	1.42	0.9980	0.4337	3.0817	0.9462

q_e (mg/g) = adsorption capacity

K_1 (1/min) = the rate constant of pseudo-first order kinetic

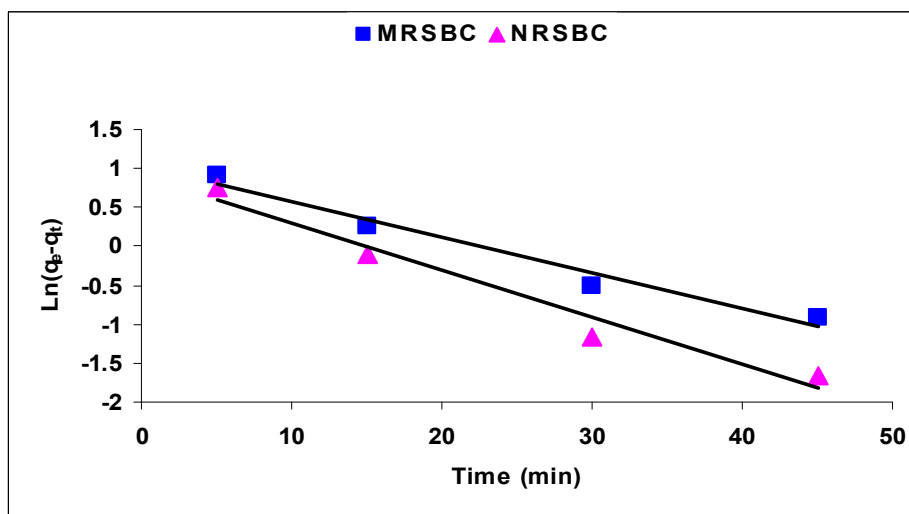
K_2 (g/mg.min) = the rate constant of pseudo-second order kinetic

h (mg/g.min) = initial adsorption rate

K_i ($\text{mg/g.min}^{1/2}$) = the rate constant of intra-particle diffusion kinetic

b (dimensionless) = intercept

Figure 9; Pseudo-first order kinetic model for the adsorption of Mn (II) on NMRSBC and MRSBC adsorbents



Regarding the amounts of correlation coefficients for three mentioned models, the amount of R^2 for pseudo-second order kinetic (for both adsorbents) is closer to 1 at compare with two models of pseudo-first order and intra-particle diffusion therefore, experimental data show more adaption with pseudo-second order kinetic.

Figure 10; Pseudo-second order kinetic model for the adsorption of Mn (II) on NMRsBC and MRSBC adsorbents

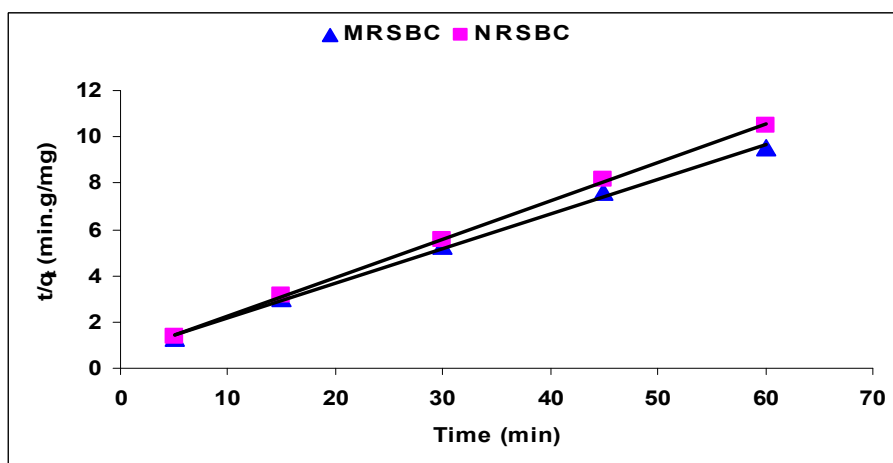
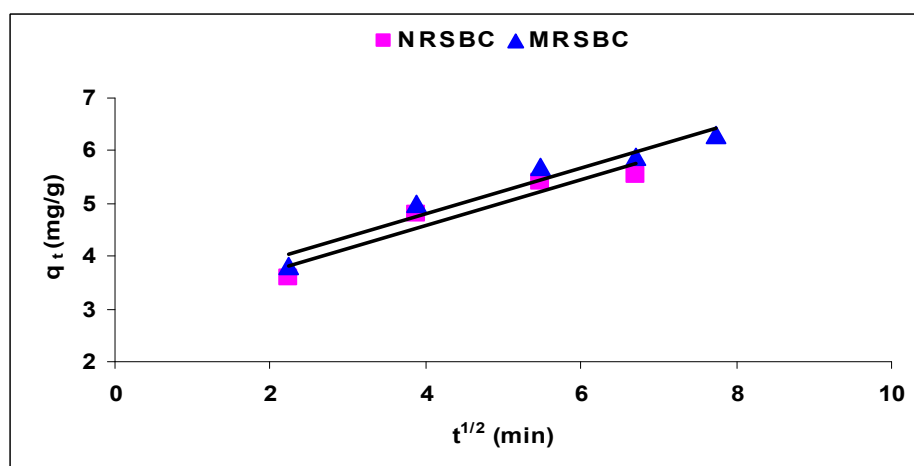


Figure 11; Intra-particle diffusion kinetic model for the adsorption of Mn (II) on NMRsBC and MRSBC adsorbents



These values of R^2 are 0.9980 and 0.9998 for both MRSBC and NMRBC adsorbents, respectively. As it shown in Table 3, the theoretical and experimental values of q_e are higher for MRSBC than for NMRBC and thus demonstrate higher sorption capacity for MRSBC. The value of R^2 (for both adsorbents) for pseudo-first order kinetic is higher than its value for intra-particle diffusion kinetic but less than pseudo-second order kinetic. The amount of intercept (b) of intra-particle diffusion kinetic is not zero (Table 3). This is further proof for lack of adhering the adsorption kinetic of Mn (II) on NMRBC and MRSBC adsorbents from intra-particle diffusion kinetic.

3.8. The effect of NMRBC and MRSBC on Mn (II) at industrial effluents

To investigate the ability of MRSBC and NMRBC to remove Mn (II) from industrial effluents, some experiments were studied on a set volume (60mL) and Mn (II) concentration (18.1mg/L) of petrochemical effluent as real sample using MRSBC and NMRBC. The optimum conditions obtained from the experiments with synthetic effluent (Table 1) were used for this experiment. The best percentage Mn (II) removal from petrochemical effluent was 95% with MRSBC which was higher than that for NMRBC (87%). According this result, the chemical modification of NMRBC and conversion that to MRSBC caused to increase the percent of Mn (II) removal from petrochemical effluent from 87% to 95%.

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