# Efficiency of Multi-Walled Carbon Nanotubes in Adsorbing Humic Acid from Aqueous Solutions

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Presence of humic acid in water resources is one of health problems of most communities. Humic Acid naturally exists in water resources and is one of precursors of trihalomethanes (THMs). In recent years, various methods have been proposed to reduce or remove humic acid. This research was carried out with the aim of reviewing the feasibility of using multi-walled carbon nanotubes (MWCNTs) as an adsorbent to adsorb humic acid from aqueous solutions.This batch study was conducted under laboratory conditions including solution initial pH, contact time, different concentrations of humic acid and different adsorbent doses. Results were analyzed using SPSS and Excel software. Results revealed that as pH decreased, humic acid adsorption level increased. The highest adsorption level occurred at pH = 4. It was also observed that optimum time to achieve maximum adsorption of humic acid and to achieve equilibrium conditions was 3 h. As adsorbent dose increased, removal efficiency increased too and as initial concentration of humic acid decreased as well as humic acid removal efficiency increased. Owing to small size, large specific surface area, crystalline form, unique network order, high reactivity and good function of multi-walled carbon nanotubes as an adsorbent in removing organic pollutants from aqueous solutions, this adsorbent can be effective in removing humic acid.

Keywords: Multi-walled carbon nanotubes, Humic acid, Adsorption.

## INTRODUCTION

Presence of natural organic matters (NOMs) in water resources has caused a lot of problems in water treatment processes, especially in conventional water treatment processes. Chlorination is the most common disinfection method in water treatment plants in most countries. Studies, carried out on water which is disinfected using chlorine compounds, have shown that due to the reaction of chlorine with natural organic matters available in water a group of chlorinated organic compounds (known as disinfection by-products) are formed[1,2]. Organic matters available in natural water originate from decomposition of plants and animals. The most common natural organic matters in surface water are humic acid and fulvic acid. Concentration of organic matters in surface water has been reported to be 10-30 mg/L. These compounds are combined with heavy metals, most of which are carcinogenic and then these hazardous compounds are transferred to water. Moreover, these compounds make a complex with pesticides, react with chlorine and create carcinogenic compounds[3-5]. Humic acid makes up 60 to 90 % of natural organic matters. Presence of organic matters in treated water results in regrowth of pathogenic microorganisms in water distribution network. Moreover, these compounds clog membrane filters and anionic resins and prevent iron and manganese oxidation[6]. Making use of activated carbon, membrane processes and advanced coagulation are the most common methods of removing trihalomethanes and their precursors[7-9]. However, these methods have some limitations, the most important of which are as follows: high utilization expenses and initial investment, clogging, excess sludge production, water pH reduction, production of highly corrosive water and the needs for reduction operation[4,5,10]. Surface adsorption process is one of the methods used to remove precursors. Generally speaking, surface adsorption is the process of collecting materials which are in a suitable solution interface. In this process, different materials (*e.g.* powdered and granular activated carbon, ash, bentonite, amyloid P, biomass, powdered activated charcoal and coal coke) have been used[3,11,12,13]. Adsorbents have been widely used to remove organic and inorganic pollutants. Of them, carbon nanotubes have had the best performance in removing pollutants due to their large specific surface, small size and multi-layer structure[14]. To remove methylene blue and methylene red, Qu *et al.*[15] applied

multi-walled carbon nanotubes coated with $Fe_2O_3$. Results showed that required time to obtain equilibrium in adsorption process was 1 h and that multi-walled carbon nanotubes were very efficient and suitable in removing these colours. Jia *et al.*[16] measured removal of acid red using single-walled carbon nanotubes and multi-walled carbon nanotubes. Research carried out to remove organic and inorganic pollutants by carbon nanotubes showed that these matters had high potential for removing organic and inorganic pollutants due to their high specific surface, small size and layered structure. The aim of this study was to remove humic acid as an organic pollutant in aqueous environment using multi-walled carbon nanotubes (MWCNTs).

## EXPERIMENTAL

In this study, humic acid produced by Aldrich-Sigma Company was used to prepare samples. Other materials are produced by German Merck Company. To remove nanotubes from solution, 0.2 μ cellulose acetate filters (produced by German Sartorius Company) were used.

Multi-walled carbon nanotubes are products of Research Institute of Petroleum Industry. To examine position of functional groups on the surface of nanotubes, scanning electron microscope (SEM), size and structure of MWCNTs using transmission electron microscopy (TEM) and nanotubes specific surface using BET method (BET) were used. To do this, data presented by Research Institute of Petroleum Industry was used. Figs. 1 and 2 show TEM and SEM image of MWCNTs. Outer and inner diameters of MWCNTs were 10-30 and 3.8 nm. Also, its length was 10 mm, its specific surface was 270 $m^2$/g and purity of consumed nanotubes was 95 %.

**Batch adsorption experiments:** Batch experiments were conducted using certain concentrations of humic acid and certain concentrations of MWCNTs. Experiments were done in 250 mL glass bottles at 23.3 °C. Bottles were placed in an incubator with rotating shakers (140 rpm). pH was adjusted for every solution using HCl and NaOH. For every sample, a control sample was prepared in test conditions. At the end of every experiment, solutions in the bottles were filtered using cellulose acetate filters (0.2 μpores) so as to determine final level of humic acid. Humic acid level was determined using UV spectrophotometers (SP-3000 Puls-Japan) with wavelength of 254 nm. Calibration curve of original and control samples were
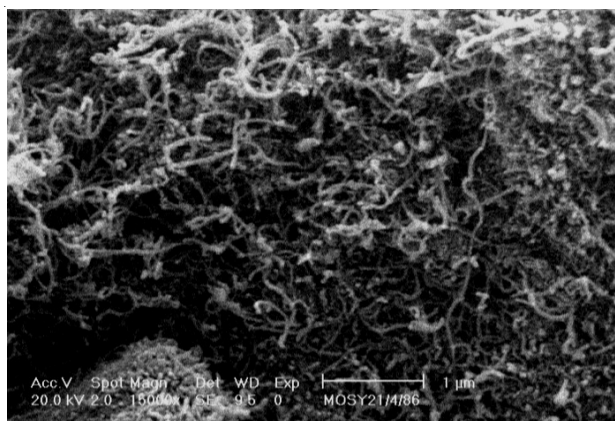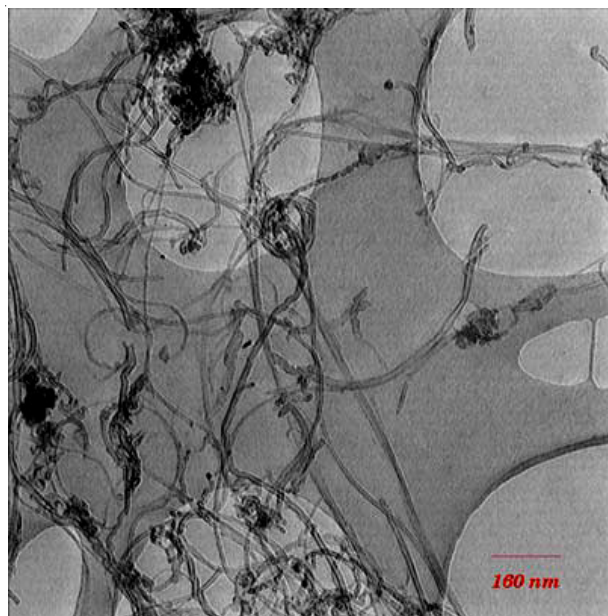

Fig. 2. TEM image of MWCNTs

achieved under similar test conditions. Levels of humic adsorbed permass unit of MWCNTs were calculated[17] by the equation $q_e$ (mg/g):

$$q_e = \frac{(C_o - C_e)}{W} \times V$$

where, V is volume of dissolved humic acid per liter; $C_0$ and $C_e$ are initial and equilibrium concentrations of humic acid (mg $L^{-1}$); and W is adsorbent mass (g).

## RESULTS AND DISCUSSION

**Effect of pH and contact time:** To study the effect of contact time and pH in adsorption process, humic acid solution with concentration of 20 mg/L and different pHs equal to 4, 7 and 10 was prepared. It was then exposed to 0.6 g/L of MWCNTs; samples were taken in different times so as to determine equilibrium time. Fig. 3 shows adsorption capacity of humic acid by MWCNTs in different times. As shown in this figure, humic acid removal level rises dramatically at the beginning but decreases at the end. Results of this stage revealed that although adsorption level increased as contact time increased, humic acid adsorption by MWCNT reached equilibrium time after 3 h and its removal remained relatively constant after this time. Results of this research match the results of other studies carried out on the effect of initial concentration of pollutant and adsorption contact time. For example, Mezenner and Bensmaili[18] studied phosphorous adsorption from iron-covered eggshell and reported that as initial concentration of pollutant and contact time increased, adsorption level and rate decreased. In this study, maximum adsorption level happened in the first 1 h and in more contact times the adsorption level decreased[18]. These changes in adsorption level in various times may be due to the fact that in initial contact times, most parts of the adsorbent surface are empty and changes in pollutant concentration are more in liquid phase. As time passes, empty sites in adsorbent surface decrease and result in reduced level of changes in liquid phase and thus reduced adsorption rate. In


Fig. 1. SEM image of MWCNTs

other words, as time passes, pollutant is adsorbed slowly in empty sites due to the increased repulsive force among molecules of the pollutant adsorbed on the adsorbent surface; it results in longer adsorption time or reduced adsorption level[19,20]. To study the effect of pH on humic acid adsorption by MWCNTs, humic acid solutions were prepared with initial concentration of 20 mg/L. These solutions were adjusted in three different pHs equal to 4, 7 and 10 using NaOH or 0.1 N HCl. Then, 0.6 g/L of adsorbent was added to every solution, they were mixed for 3 h and samples were taken in different time intervals; solution was filtered using cellulose acetate filter paper (0.2 μm pores). Finally, level of the remaining humic acid was evaluated. As shown in Fig. 3, pH = 4 is suitable for removing humic acid by MWCNTs. According to Fig. 3, humic acid removal is more effective in acidic pH than in neutral or alkaline (pH = 7) and alkaline (pH = 11). Therefore, efficiency of humic acid removal was 94.1 % for synthetic wastewater with initial concentration of 20 mg/L, time of 3 h, adsorbent concentration of 0.6 g/L and pH = 4. Solution pH is an important parameter in adsorption process because it affects the interaction between functional groups of adsorbent and adsorbed matter. High adsorption of humic acid in acidic pH is as a result of humic acid size and molecular structure which changes into spherical structure in acidic pHs; in higher pH, it changes to linear or elongated structure which results in reduced humic acid adsorption[20,21].
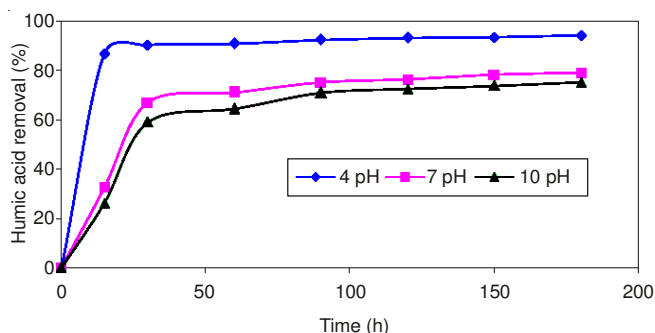


Fig. 3.  Effect of contact time and pH on humic acid removal by MWCNTs (humic acid: 20 mg/L, MWCNTs dose: 0.6 g/L)

**Effect of initial concentration of humic acid:** To study the effect of humic acid concentration on adsorption, humic acid solutions were prepared with concentration of 5-30 mg/L and pH = 4. Then, the effect of various contact times was examined on 0.6 g/L of adsorbent (Fig. 4). Level of humic acid removal was 97 and 92 % in concentrations of 5 and 30 mg/L, respectively. In other words, as initial concentration of humic acid decreases, removal efficiency (by a constant dose of adsorbent) increases.

Results show that humic acid adsorption level is a function of its initial concentration. Humic acid initial concentration provides an important driving force to overcome mass transfer resistance between solid phase and solution phase. Owing to very high portions of active adsorption sites available on adsorbent in lower initial concentrations, increased initial concentration results in increased humic acid adsorption level[22]. As humic acid initial concentration increases, adsorption level increases too. Results obtained in this step conform to a study
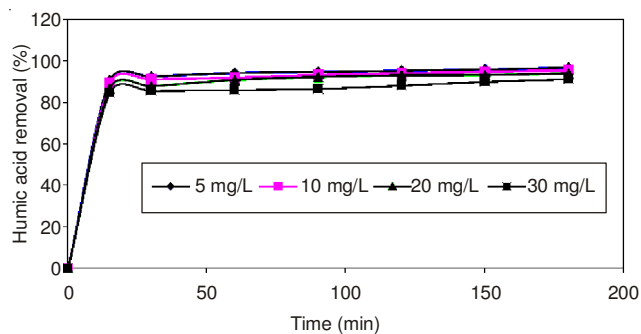


Fig. 4.  Effect of initial humic acid concentrations on humic acid adsorption (MWCNTs dose: 0.6 g/L, pH: 4)

carried out by Wang et al.[22] for removal of fulvic acid from aqueous solutions using surfactant-modified zeolite. The findings showed that removal of fulvic acid increased as concentration increased and that concentration reached equilibrium condition after 2 h. Results also revealed that fulvic acid adsorption level was a function of its initial concentration. Moreover, increased initial concentration increased interaction between adsorbent and fulvic acid[22]. Lu and Su[23] studied adsorption of natural organic matters by carbon nanotubes. In this research, adsorption level increased as initial concentration of natural organic matters increased[23].

**Effect of adsorbent dose:** To study the effect of adsorbent dose on adsorption process, samples were prepared with a volume of 100 mL and initial concentration of 20 mg/L; then, different doses of adsorbent (0.2-1g/L) were added to them. Samples were mixed in the shaker for 24 h and concentration of the remaining humic acid was measured. Results are shown in Fig. 5. Results of this step revealed that as adsorbent mass increased from 0.2 to 1 g/L, level of humic acid remained in the solution decreased from 1.56 to 0.14 mg/L; accordingly, humic acid removal efficiency increased from 92 to 100 %.
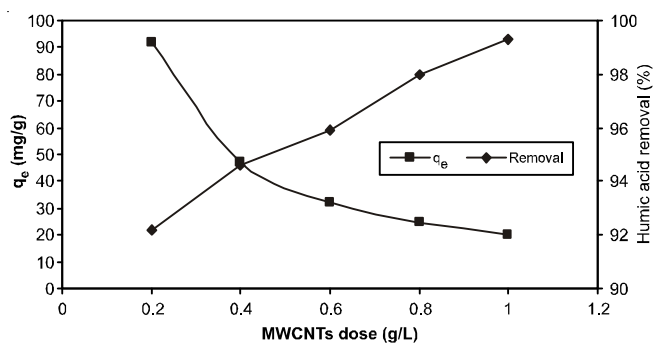


Fig. 5.  Effect of MWCNTs dose on adsorption of humic acid (humic acid: 20 mg/L, pH: 4 and 24 h contact time)

According to results of this stage, adsorption efficiency increased and the remaining humic acid decreased as adsorbent level increased. However, as adsorbent level increased from 0.2 to 1 g/L, level of pollutant adsorbed in adsorbent mass unit decreased from 92.2 to 19.86 mg/g.

Increased level of humic acid adsorption is as a result of increased adsorbent dose and thus increased active and effective adsorption level. Although increased dose of adsorbent results in increased humic acid removal efficiency, its adsorption level decreases in adsorbent mass unit because some active points

on adsorbent surface remain unsaturated and entire capacity of adsorbent is not used[24]. Results of this study and other studies showed that increased dose of adsorbent resulted in less relative increase in humic acid adsorption and in reduction of level of pollutants adsorbed in adsorbent mass unit. This phenomenon is associated with not making use of adsorbent entire capacity[25]. Askari *et al.*[26] studied performance of hexadecyltrimethyl-ammonium bromide (HDTMA-Br)-modified zeolite in removing humic acid from aqueous solutions. Results showed that as adsorbent dose increased, removal efficiency increased. Removing humic acid by modified zeolite follows from first order kinetics[26].

**Adsorption isotherm experiments:** Isotherm equations are used to describe experimental data. Analysis of data resulted from adsorption isotherm is very important to obtain an equation which explains level of correlation between results. To define the reaction between adsorbent and the adsorbed material, different types of linear and non-linear adsorption isotherms were examined (Figs. 6-8).
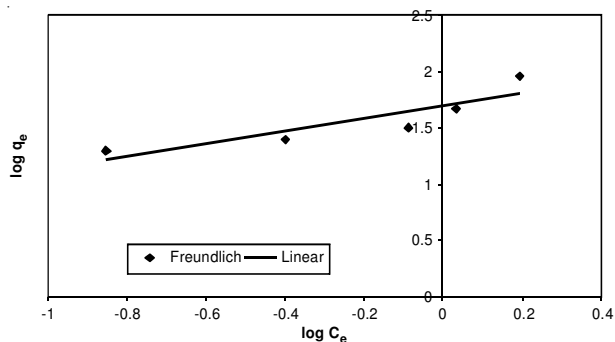


Fig. 6. Freundlich isotherm linear form for the adsorption of humic acid onto the MWCNTs
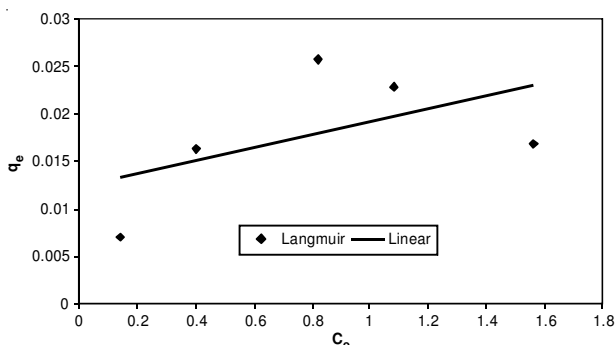


Fig. 7. Langmuir Isotherm linear form for the adsorption of humic acid onto the MWCNTs
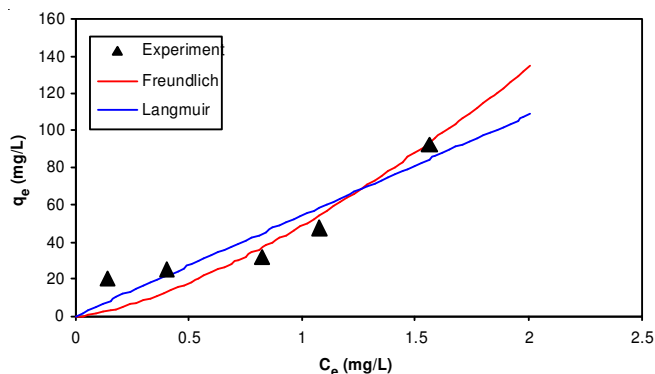


Fig. 8. Non-linear of Langmuir and Freundlich for the adsorption of humic acid by MWCNTs

In the present study, the best fit of an isotherm to the experimental data was tested using the value of coefficient of determination ($r^2$), which is defined as eqn. 1.

$$r^2 = \frac{\Sigma(q_m - \overline{q}_e)^2}{\Sigma(q_m - \overline{q}_e)^2 + \Sigma(q_m - q_e)^2} \tag{1}$$

where, $q_m$ is the equilibrium capacity obtained from isotherm model, $q_e$ is the equilibrium capacity obtained from experiment and $\overline{q}_e$ is the average of $q_e$.

The average percentage errors (APE) is calculated according to eqn. 2 indicated the fit between the experimental and predicted values of adsorption capacity used for plotting isotherm curves:

$$APE\ (\%) = \frac{\Sigma_{i=1}^{N}\left|((q_e)_{experimental} - (q_e)_{predicted})/(q_e)_{experimental}\right|}{N} \times 100$$

where, N is the number of experimental data.

According to the results and explanation of studies, non-linear Freundlich isotherm has the most consistency in adsorbing humic acid by multi-walled carbon nanotubes ($r^2 = 0.91$). Table-1 shows parameters obtained from linear and non-linear isotherm studies.

| TABLE-1 ISOTHERM PARAMETERS OBTAINED FROM HUMIC ACID ADSORPTION ON MWCNTS | | | |
|---|---|---|---|
| Isotherm type | Isotherm parameter | Linear | Non-linear |
| Freundlich | 1/n | 0.56 | 1.46 |
| | $K_F$ | 41.11 | 48.66 |
| | $r^2$ | 0.57 | 0.91 |
| | APE (%) | 23.06 | 32.76 |
| Langmuir | $Q_m$ | 144.93 | 31568.67 |
| | $K_L$ | 0.56 | 0.0017 |
| | $r^2$ | 0.69 | 0.88 |
| | APE (%) | 28.01 | 28.93 |

**Non-linear isotherms method:** For non-linear method, a trial and error procedure, which is applicable to computer operation, was used to determine the isotherm parameters by minimizing the respective coefficient of determination between experimental data and isotherms using the solver add-in with Microsoft's spreadsheet, Microsoft excel. The result of non-linear isotherms method is presented in Table-1.

**Adsorption kinetic experiments:** To study kinetics of humic acid adsorption onto MWCNTs, study data, concentration of humic acid (20 mg/L) and adsorbent dose (0.06 g/100 mL) were examined and conformity of results to models pseudo first order, Pseudo second order, Elovich, diffusion intraparticle was examined. Results are shown in Table-2. Results revealed that kinetics of humic acid adsorption onto MWCNTs follows from pseudo second order kinetics ($R^2 = 0.99$). Results obtained from adsorption kinetics are shown in Figs. 9-12. Table-3 shows summary of parameters calculated for different kinetic models in humic acid adsorption using MWCNTs.

## Conclusion

In this research, we examined the effect of initial concentration, contact time, pH, humic acid initial concentration and adsorbent dose on removal of humic acid by MWCNTs. Results showed that as contact time increased, humic acid adsorption

TABLE-2
EQUATION AND LINEAR FORM OF KINETICS

| Kinetic | Equation | Linear form | References |
|---|---|---|---|
| Pseudo first order | $\dfrac{dq_t}{dt} = k_1(q_e - q_t)$ | $\log(q_e - q_t) = \log(q_e) - \dfrac{k_1}{2.303}t$ | |
| Pseudo second order | $\dfrac{dq_t}{dt} = k_2(q_e - q_t)^2$ | $\dfrac{t}{q_t} = \left(\dfrac{1}{k_2 q_e^2}\right) + \left(\dfrac{1}{q_e}\right)t$ | 27, 28, 29 |
| Elovich | $\dfrac{dq_t}{dt} = \alpha \exp(-\beta q_t)$ | $q_e = \left(\dfrac{1}{\beta}\right)\ln(\alpha\beta) + \left(\dfrac{1}{\beta}\right)\ln t$ | |
| Intraparticle diffusion | - | $q_t = K_{dif} t^{0.5} + C$ | |

TABLE-3
PARAMETERS OBTAINED FROM VARIOUS
KINETICS MODELS FOR THE ADSORPTION
OF HUMIC ACID BY MWCNTS

| Kinetic | Parameter | pH 4 | pH 7 | pH 10 |
|---|---|---|---|---|
| Pseudo first order | $k_1$ | 0.016 | 0.021 | 0.019 |
| | $q_e$ cal | 4.59 | 13.15 | 14.63 |
| | $R^2$ | 0.51 | 0.79 | 0.84 |
| Pseudo second order | $k_2$ | 0.026 | 0.0037 | 0.0023 |
| | $q_e$ cal | 31.45 | 2.82 | 1.66 |
| | h | 25.71 | 2.28 | 1.31 |
| | $R^2$ | 0.99 | 0.99 | 0.98 |
| Elovich | $\alpha$ | 15.92 | 5.57 | 6.14 |
| | $\beta$ | 0.17 | 0.18 | 0.19 |
| | $R^2$ | 0.82 | 0.94 | 0.94 |
| Intraparticle diffusion | $K_{dif}$ | 1.77 | 1.88 | 1.85 |
| | C | 12.72 | 5.08 | 3.74 |
| | $R^2$ | 0.56 | 0.81 | 0.85 |



Fig. 11. Elovich kinetic for the adsorption of humic acid by MWCNTs



Fig. 12. Intraparticle diffusion kinetic for the adsorption of humic acid by MWCNTs
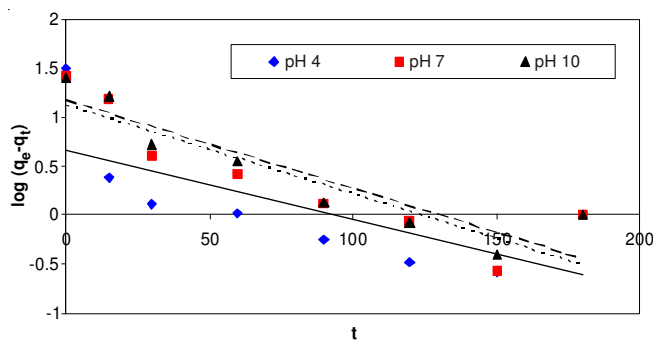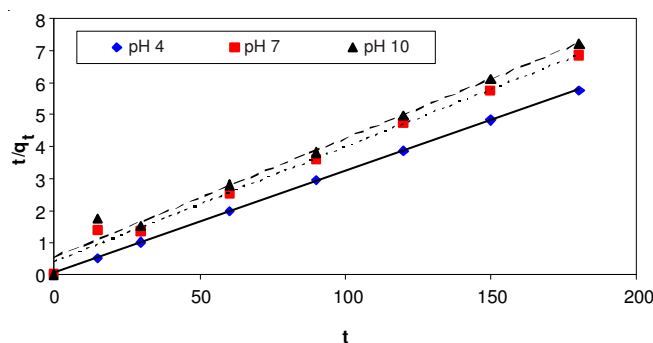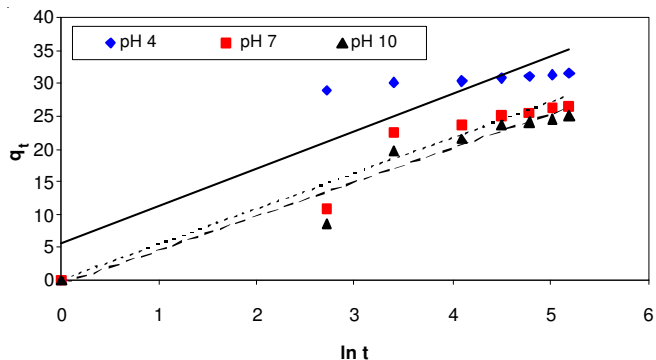


Fig. 9. Pseudo first order kinetic for the adsorption of humic acid by MWCNTs
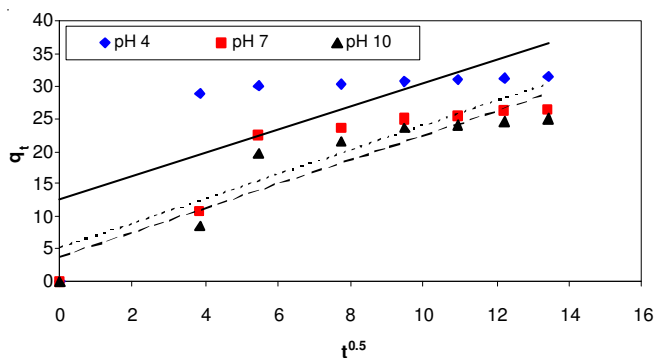


Fig. 10. Pseudo second order kinetic for the adsorption of humic acid by MWCNTs

level increased too and equilibrium condition was reached after 3 h. In this research, pH = 4 was suitable for removing humic acid by MWCNTs. Also, as initial concentration increased, humic acid adsorption capacity increased too, with maximum adsorption being 96.8 %. Results revealed that increased adsorbent dose resulted in increased removal efficiency; maximum adsorption capacity was 31.37 mg/g. Humic acid adsorption by MWCNTs follows pseudo second order kinetics. Owing to their small size, huge surface area, crystalline form, unique network order, high reactivity and considerable performance, MWCNTs can be highly used as adsorbents to remove organic pollutants, especially humic acid, from aqueous solutions.

### Nomenclature

$R^2_y$    Correlation between measured and simulated data

AICc    Corrected akaike information criterion

$R^2_N$    Normal probability correlation coefficient

$M^2$    Linssen index

| | |
|---|---|
| $A_T$ | Temkin constant (L/g) |
| $B_T$ | Constant related to heat of adsorption (mg/L) |
| C | Thickness of the boundary layer (mg/g) |
| $C_0$ | Initial concentration (mg/L) |
| $C_e$ | Equilibrium concentration in solution (mg/L) |
| Cs | Saturation concentration in solution (mmol/L) |
| $C_t$ | Equilibrium concentration in solution at time t (mg/L) |
| h | Initial sorption rate (mg/g min) |
| $k_1$ | Pseudo first-order rate constant (L/ min) |
| $k_2$ | Pseudo second-order rate constant (mg/g min) |
| $K_B$ | BET constant |
| $K_{dif}$ | Intraparticle diffusion rate constant (mg/g min$^{0.5}$) |
| $K_{D-R}$ | Adsorption energy (mol$^2$/kJ$^2$) |
| $K_f$ | Freundlich isotherm constants (L/g) |
| $K_G$ | Saturation constant (mg/L) |
| $K_L$ | Langmuir isotherm constants (L/mg) |
| n | Adsorption intensity |
| $N_b$ | Cooperative binding constant |
| $q_e$ | Equilibrium adsorbent concentration on adsorbent (mg/g) |
| $q_e$ cal | Calculated values of $q_e$ (mg/g) |
| $Q_m$ | Maximum monolayer capacity (mg/g) |
| $q_t$ | Adsorbed concentration at time t (mg/g) |
| R | Universal gas constant, 8.314 J/mol K |
| $R^2$ | Correlation coefficients |
| $R_L$ | Dimensional separation factor |
| T | Absolute temperature in Kelvin |
| α | Initial adsorption rate (mg/g min) |
| β | Desorption constant (g/mg) |
| ε | Polanyi potential |

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