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Removal of Bisphenol, Using Antimony Nanoparticle Multi-walled Carbon Nanotubes Composite from Aqueous Solutions

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ABSTRACT

This study focuses on preparing Antimony Nanoparticle Multi-walled Carbon (ANMWC) composite as an effective adsorbent and then the effect of produced composite in BPA removal from aqueous solutions was studied. ANMWC were prepared using chemical method and characterized with X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and Brunauer–Emmett–Teller (BET). Moreover, the removal efficiency of prepared AMWCNT and Nanoparticle Multi-walled Carbon (MWCNT) in removal of Bisphenol A was investigated. Results revealed that the BPA removal efficiency by AMWCNT increased from 80 to 93 % with the increase of contact time 5 to 60 min. The maximum removal efficiency for the both adsorbents was seen at pH 7, which was 85% for MWCNT and 95% for ANMWC composite. According to the results obtained, pH_{zpc} for both adsorbents was 7. Results showed that the adsorption process followed the pseudo-first order model with a high correlation value and BPA adsorption on MWCNT followed the Langmuir isotherm model.

Keywords: Bisphenol, Adsorption, Nanoparticle Multi-walled Carbon Nanotubes, composite.

INTRODUCTION

Bisphenol A (BPA) is one the most widely used chemical compounds as a raw material in the product of polycarbonate and epoxy resins [1]. BPA can release into the environment through its use and handling, and permitted discharges [2]. Recently, this compound and its derivatives have been found to be widely distributed in the natural environment, as well as in surface water [3]. Due to the high toxicity of phenolic compounds to humans, their removal has been taken a huge attention of many researchers[4].

In recent years, nanotechnology has been taken into huge consideration as a promising technology to treat water. According to the literature, Multi-walled carbon nanotubes (MWCNTs) have shown an ability to efficiently remove various organic pollutants such as dioxins, polychlorinated dibenzo-furans and biphenyls from aqueous environments[5, 6].

Nowadays, considerable efforts have been made to produce metal-carbon nanocomposite materials, not only because the carbonic compound improves the mechanical properties of the composites, but also because the produced composites possess the properties of individual components with a synergistic effect [7, 8].

Therefore, the present work focuses on preparing ANMWC composite as an effective adsorbent and then the effect of produced composite in BPA removal from aqueous solutions was studied. ANMWC were prepared using chemical method and characterized with X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and Transmission *Electron Microscope* (TEM).

MATERIALS AND METHODS

Chemicals

Bisphenol-A was obtained from Merck (Germany). The MWCNT used in this study was obtained from Nutrieno Co. (Tehran, Iran, http://parscenter.com/Company/CMP645327). Sodium dodecyl sulfate, Antimony powder, Sodium sulfate anhydrous, Sodium hydride powder, Sodium Borohydride powder and other chemicals were purchased from Merck.

Table 1: Characteristics of MWCNTs

Parameter	Unit	Amount
Appearance	-	Black powder
External diameter	nm	20-30
Length	µm	30
Purity carbon	%	95
specific surface area	m^2/g	110
Density	g/cm^3	2.1

Preparation and Characterization of adsorbents

To produce Antimony Nanoparticle Multi-walled Carbon (ANMWC) composite Ultrasonic device was used. The device consist of a stainless steel reactor equipped with a transformer and an ultrasonic wave generator. Table 2 shows the characteristics of used Ultrasonic device.

To prepare ANMWC composite, 100 mg of nanoparticle multi-walled carbon and 40 mg of sodium dodecyl sulfate (as surfactant) were dissolved in 100 ml of pure ethanol. The solution was mixed by Ultrasonic device for 20 min. Next, 80 mg of Sodium Borohydride was added to the solution. Again, the mixtures were mixed for 20 min. Then Antimony solution (17.5 mmol/L) were gradually added to the nanoparticle multi-walled carbons. Finally, the products were placed into the Ultrasonic devise for 1 h under stirring conditions. The products were then filtered and washed with doubly distilled water and then dried at 60°C in an oven for 12 h[9].

In order to obtain the characterization of adsorbent X-Ray Diffraction (XRD, ITALSTRUCTRE, model ADP 2000, Italy) was used. Fourier Transform Infrared Spectroscopy (FTIR, Perkin Elmer Spectrum) was employed in order to determine the functional groups and the chemical structure on surface area of adsorbent materials before and after modification.

Table 2: Characteristics of used Ultrasonic device

model	LUC-405
time	0-99 min
temperature	0-50 0c
Frequency	40 KHZ
capacity	5 L
volume capacity	300×55×150 mm
useful volume	300×285×255 mm
power	350
chamber material	Stainless steel
devise body material	ABS
country	Korea
voltage	100 to 240v-AC, 50/60Hz

Moreover, Transmission Electron Microscope (TEM) was used in order confirm the adsorbent modification. Moreover, pHzpc of the synthesized composite and nanoparticle multi-walled carbon was determined using the pH drift method[10].

Batch experiments

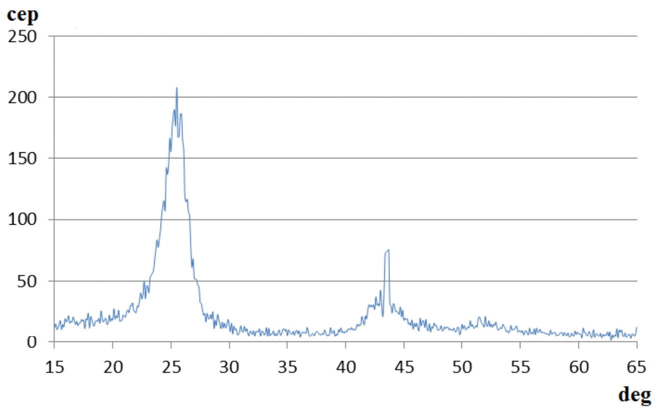
To determine the optimum conditions for BPA removal by ANMWC composite, the effect of some operational parameters on the adsorption efficiency was studied. Experimental stages are summarized in Table 3[10-14].

BPA residual concentration

After adsorption process BPA residual concentration was measured using a spectrophotometer (Uv/Vis spectrometer-DR 5000, Germany) at a wavelength of 276 nm[15,16]. Eventually,

Table 3: Experimental set-up (experiment steps)

Parameters		Unit	Range
1	Contact time	min	50, 80, 100, 150 and 200
2	pH	-	3, 7 and 10
3	Synthesized adsorbent concentration	mg/L	100, 200 and 400
4	Initial BPA concentration	mg/L	20, 60 and 100



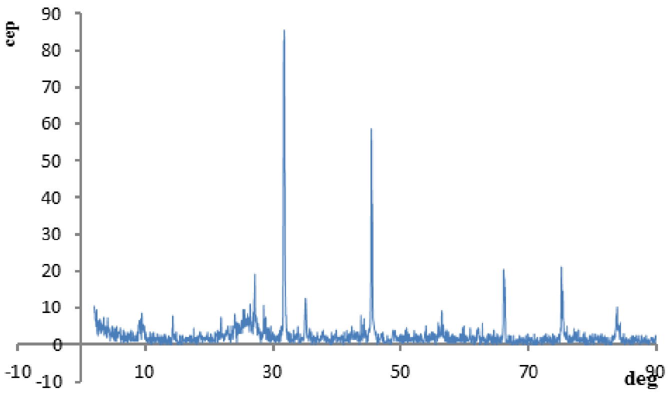


Fig. 1: XRD patterns of (a) MWCNT (b) ANMWC composite

BPA efficiency was calculated according to the following equation[12].

$$R(\%) = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \qquad ...(1)$$

C_0: initial concentration of the BPA (mg/L)
C_t: instant concentration of the BPA (mg/L)
R%: Percentage of BPA removal

RESULTS AND DISCUSSION

The XRD patterns are shown in fig.1 (a, b). As can be seen in fig.1 (a), a peak around 25 indicated the presence of carbon, the peak around 43, indicated the presence of oxygen and peaks between 65 and 85 indicated the presence of antimony. Fig. 1 (b) and the presence of antimony element in the composition of MWCNTs confirms the claim that the ANMWC composite was properly prepared. This result is consistent with the finding of Fernando *et al*[9].

Characterization of adsorbents

Fig. 2 shows the FTIR spectra of both adsorbents (MWCNT and ANMWC composite) before and after adsorption process. As revealed, a broad peak around 3400 cm^{-1} correspond to the presence of O-H groups on the MWCNT surface. This figure showed peaks at 1623 and 1637 cm^{-1} which indicted the presence of aromatic structures C=O in the MWCNT. These results are consistent with the results of the FTIR spectrum obtained by Zazoli et al. on the application of L-cysteine functionalized single-walled carbon nanotubes for removing mercury from aqueous solutions[15]. After adsorption process a peak around 1223 cm^{-1} indicated the presence of phenolic band C-O, which indicated that BPA has been

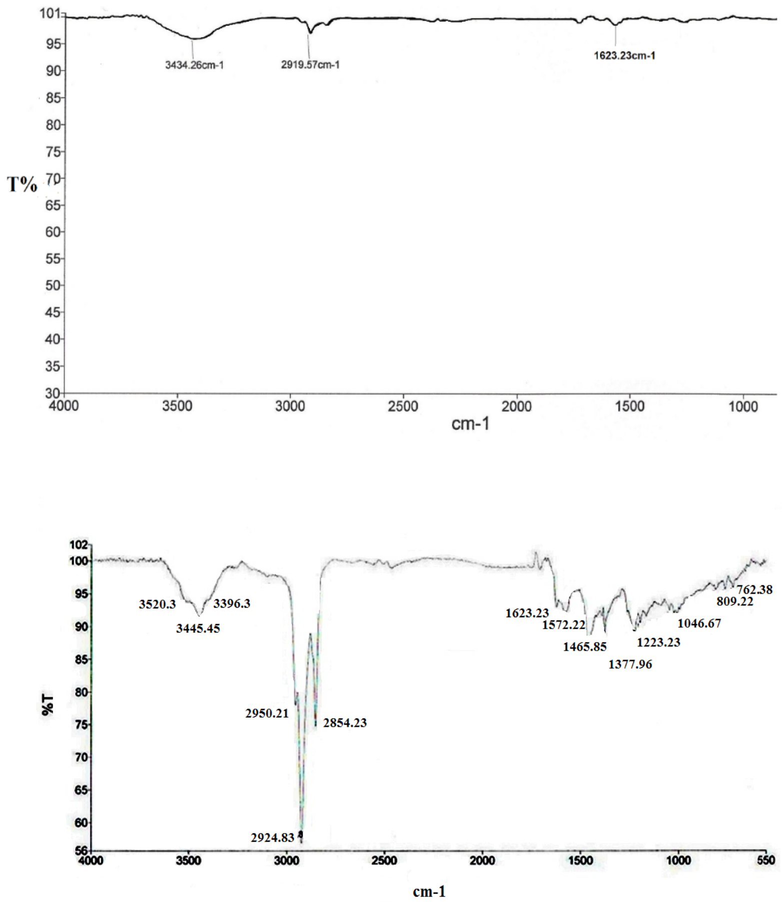


Fig. 2: FTIR spectra of MWCNT (a) before and (a) after adsorption process

adsorbed on the adsorbent surface. In spectrum of the carbon nanotubes modified with antimony, a peak at 2400 cm^{-1} indicated the presence of C-H stretching. Fig. 4 shows the TEM spectra of MWCNT and ANMWC composite. As revealed antimony particles have been located well on the MWCNT surface.

Contact time

Contact time is one of the most important parameters in adsorption process. Considering that the adsorption process is one of equilibrium reactions, so the contact time plays an important role in reaction progress. As the adsorbates can easily access to absorption sites, the process requires less contact time to reach its maximum absorption [18,19]. On the other hand, as the adsorbates cannot easily access to the adsorption sites, required contact time increased. Fig. 5 shows the effect of contact time on adsorption efficiency. Results revealed that the BPA removal efficiency by MWCNT increased from 51 to 87 % with the increase of contact time 5 to 60 min. In the mentioned range of contact time, the ANMWC composite efficiency in BPA removal increased from 80 to 93 %. As can be seen, the efficiency of ANMWC composite was better in BPA removal than that of MWCNT alone. This can be related to the influence of Antimony coated on the MWCNT surface. Dehghani et al. suggested that BPA removal increased with increasing contact time, which is in line with our result [14]. This result is also consistent with the finding of Samadi *et al*[20].

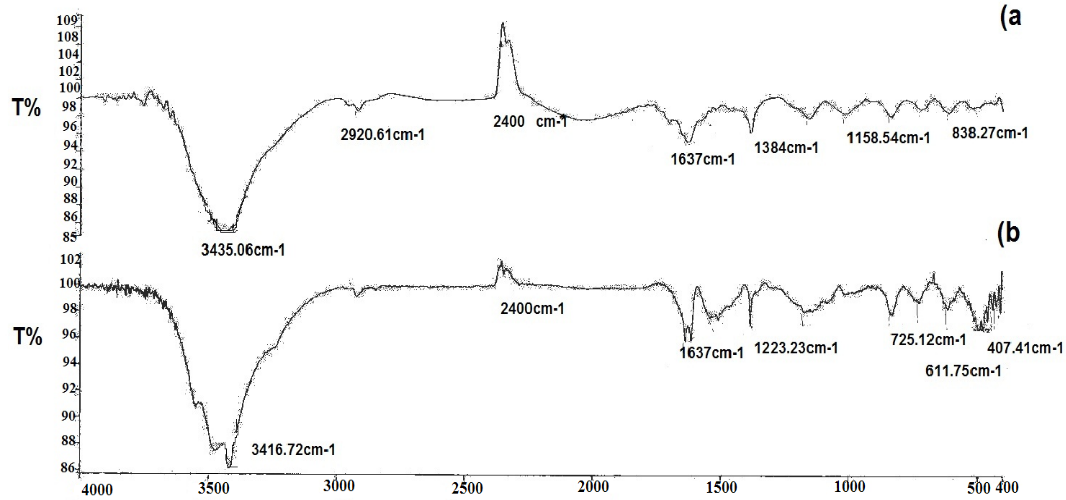


Fig. 3: FTIR spectra of ANMWC composite (a) before and (a) after adsorption process

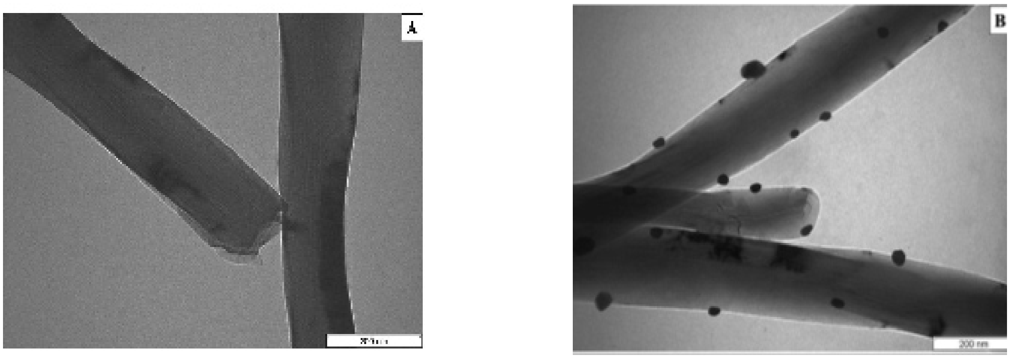


Fig. 4: TEM spectra of (a) MWCNT and (b) ANMWC composite

Effect of solution pH

Due to the direct effect of solution pH on the adsorbent surfaces and the degree of ionization of pollutants, it considered as the most important parameter in adsorption process [21]. Theoretically, pH can be affected on BPA absorption. As shown in fig.5, at acidic conditions, the removal efficiency of BPA increased gradually with increasing pH. The maximum removal efficiency was seen at pH 7, which was 85% for MWCNT and 95% for ANMWC composite. By contrast, with increasing pH values from 7 to 10, the removal efficiency for both adsorbents decreased obviously. This can be attributed to the structure and pH_{zpc} of adsorbent. According to the results obtained, pH_{zpc} for both adsorbents was 7. When the pH of the solution is higher than the pH_{zpc}, absorbent surface becomes negatively charged and can adsorb well cations by the electrostatic reactions. On the other hand, at pH values higher than the pH_{zpc}, absorbent surface becomes positively charged and absorbs well anions. Considering the negative charge of BPA surface at alkaline conditions, the adsorption rate of BPA decreased. In contrast, because of positive charge of BPA at acidic conditions, the adsorption rate of BPA increased. In addition, at alkaline pH, the degradation of OH^- groups of phenolic compounds such as BPA, prevents the formation of hydrogen bonds between adsorbed BPA molecules on the surface of the nanotubes and molecules dissolved in solution and as a result, adsorption efficiency decreased [22].

Adsorption Isotherms and Kinetics Models

According to the results, the correlation coefficient (R^2) for both the absorbents in pseudo-first order model was relatively low. So, the pseudo-first order model did not fit with the experimental data well. Results showed that the adsorption process followed the pseudo-first order model with a high correlation value. Pseudo-first order model is in accordance to the adsorption capacity and it is used when the adsorption occurs using diffusion mechanism through a boundary layer. The pseudo-second order model showed that the chemical adsorption mechanism is dominant and controller and acts as a moderator in the adsorption process [19].

In the present study, Langmuir and Freundlich isotherm models were investigated and the results of this stage are shown in Table 4. As can be seen here, in BPA adsorption on MWCNT, the correlation coefficient of Langmuir isotherm model (0.96) was higher than Freundlich isotherm model (0.82). Therefore, BPA adsorption on MWCNT followed the Langmuir isotherm model. Langmuir isotherm is the most common used isotherm to investigate the adsorption processes. This isotherm is based on the single-layer adsorption [23]. This isotherm indicated that adsorbate molecules were adsorbed on the specific points of adsorbent surface, which are called absorption sites.

The energy of adsorbates in each of adsorption sites is same and this not attributed to the presence or absence of adjacent adsorbed molecules. This assumption suggested that the energy levels are quite the same. Adsorption process is topically and occurred by colliding the adsorbates with empty sites. Finally, desorption rate depends only on the amount of material adsorbed

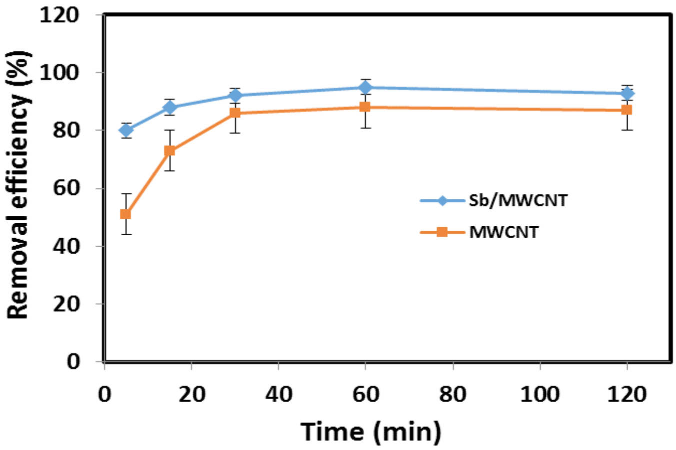


Fig. 5:

on the surface [19]. a and b are Langmuir parameters, which indicated the maximum absorption capacity and correlation energy. While, the main feature of Langmuir isotherm is a dimensionless parameter called equilibrium (R_L). The effectiveness of adsorption process in Langmuir model is determined by these parameters. $0<R_L<1$ indicate the suitable absorption, $1<R_L$ indicate unsuitable adsorption, and $R_L=0$ indicate irreversible absorption [24.] According to the R_L value (0.046), which was obtained from the calculations (Table 4), the absorption process of BPA on MWCNT was a suitable process.

According to the results, the correlation coefficient of Freundlich isotherm model (n=0.93) for the BPA absorption on ANMWC composite was higher than correlation coefficient of Langmuir isotherm model (0.81). As a result, the adsorption process followed the Freundlich isotherm model. Freundlich model defines the adsorption of adsorbates on heterogeneous surfaces and states that the adsorbates are adsorbed on the adsorbent as multi-layer. K_f and n are the constants, which are related to the adsorption capacity and absorption rate. The values of n<1 indicate unsuitable adsorption, 1<n<10 indicate a suitable adsorption, n>1 indicate stronger interactions between the absorbent and adsorbate, and n=1 indicates that the adsorption energy is the same for all sites (25). According to the n value (n=1.36), BPA absorption on ANMWC was suitable and there was a moderately strong interaction between adsorbate and adsorbent.

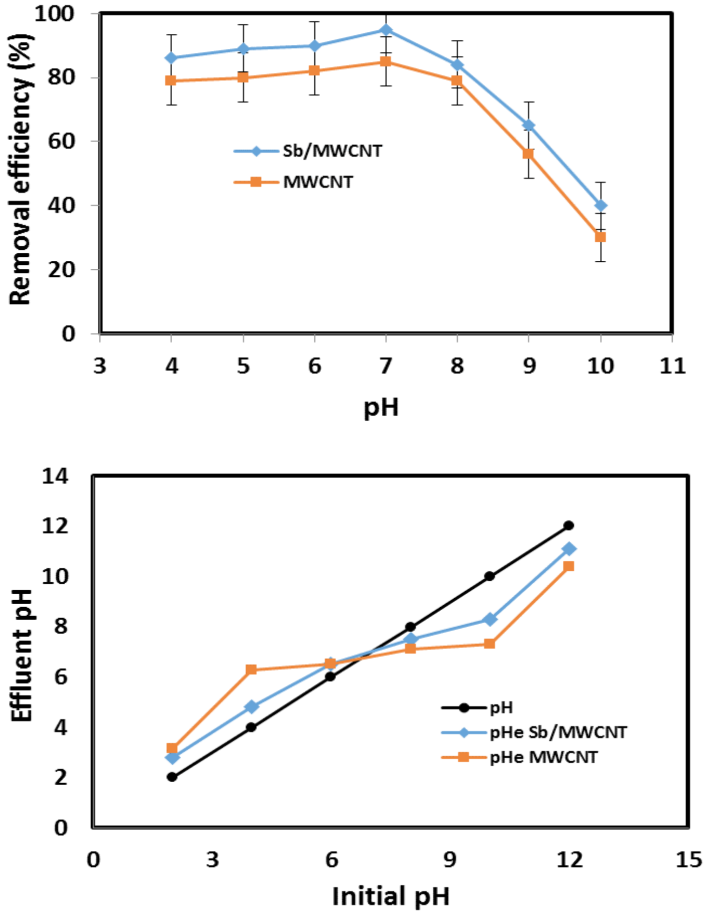
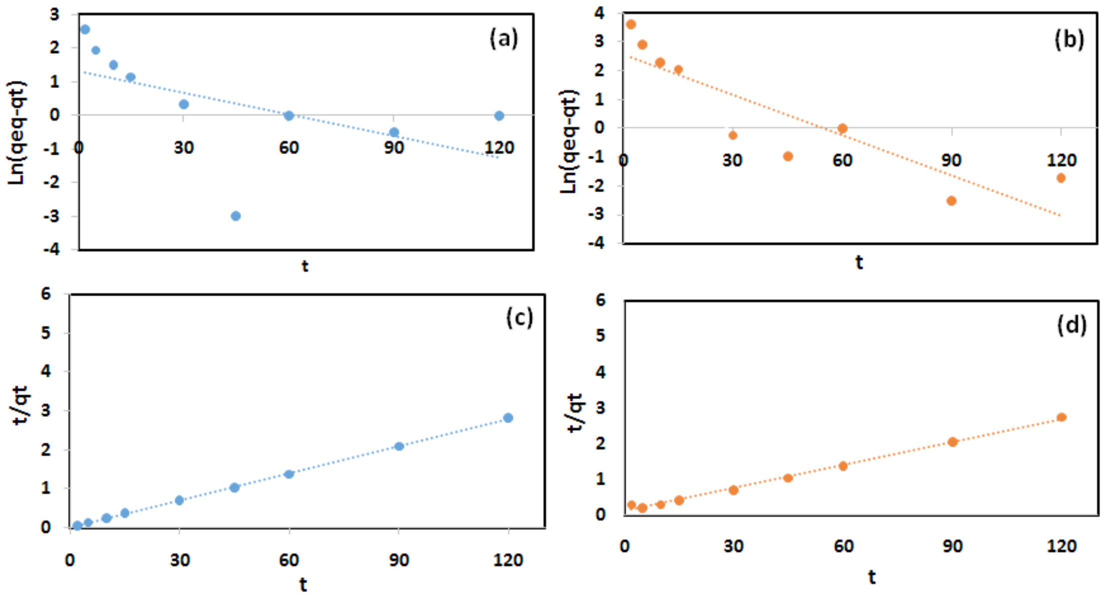


Fig. 6



	A pseudo order knitic		Pseudo-two order knitic	
	K_1	R^2	K_2	R^2
MWCNT	0.021	0.291	0.023	0.999
Sb/MWCNT	0.046	0.779	0.021	0.995

Fig. 7

CONCLUSION

The present focuses on preparing ANMWC composite as an adsorbent and then the effect of produced composite and MWCNT in BPA removal from aqueous solutions was studied. ANMWC were prepared using chemical method and characterized with X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and Transmission *Electron Microscope* (TEM). Results revealed that the BPA removal efficiency by ANMWC increased from 80 to 93 % with the increase of contact time 5 to 60 min. The maximum removal efficiency was seen at pH 7, which was 85% for MWCNT and 95% for ANMWC composite. According to the results obtained, pH_{zpc} for both adsorbents was 7. Results showed that the adsorption process followed the pseudo-first order model with a high correlation value and BPA adsorption on MWCNT followed the Langmuir isotherm model. According to the results, the both MWCNT and ANMWC composite are effective for removing pollutants from aqueous solutions. Moreover, the ANMWC composite can be used as a suitable and new adsorbent for removing organic pollutants from water environments.

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