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APPLICATION OF ADSORPTION FOR THE TREATMENT OF PHARMACEUTICAL INDUSTRIAL EFFLUENT: REMOVAL OF ATROPINE SULFATE (ATS) BY MULTIWALLED CARBON NANOTUBES

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ABSTRACT

Pharmaceutically active compounds undergo metabolic processes in organisms. Significant fractions of the parent compound are excreted in unmetabolized form or as metabolites (active or inactive) into raw sewage and wastewater treatment systems. The adsorption of atropine sulfate (ATS) onto multiwalled carbon nanotubes (MWCNTs) from aqueous solutions was studied, and the influence of contact time, adsorbent dosage, pH, and concentration of ATS. The equilibrium adsorption data were found fit Langmuir and Freundlich adsorption isotherms, pseudo-first and second order kinetics and it was also concluded that intra-particle diffusion was not the only rate controlling step.

KEY WORDS : Adsorption, MWCNT, Atropine sulfate, Kinetics, Isotherm, Intra-particle diffusion

INTRODUCTION

The release of pharmaceuticals, antibiotics and their metabolites into the aquatic environment has become an increasing concern over recent years. It is now well established that pharmaceuticals and human hormones are ubiquitous contaminants of wastewater effluents. Several studies show that many pharmaceuticals are not completely removed during wastewater treatment and as a result, this has led to their presence reported in effluents, rivers and lakes, and of course; more rarely in groundwater (Ternes, 2001; Roberts and Thomas, 2006; Gros *et al.*, 2010; Jelic *et al.*, 2011).

CNTs based nanotechnologies have attracted significant attraction in a variety of scientific fields. CNTs showed excellent sorption capability with high sorption efficiency than that of conventional granular activated carbon, graphene, and amorphous carbon. The structural properties of CNTs show a strong interaction with organic molecules via non-covalent forces such as hydrogen bonding, ð-ð stacking, electrostatic forces, Van der Waals forces, and hydrophobic interaction (Mubarak *et al.*, 2013; Das *et al.*, 2014; Wu *et al.*, 2015; Lee *et al.*, 2018). These unique and tunable properties of CNTs are used to remove several pollutants like dyes, heavy metals, pesticides, chemicals, etc. (Gopalakrishnan *et al.*, 2015; Mubarak *et al.*, 2016; Anastopoulos *et al.*, 2017).

Preparation of surface modified MWCNTs and their use in environmental pollution remediation was studied by various researchers (Yanyan *et al.*, 2018; Ncibi and Sillanpää, 2015; Mashayekh-Salehi and Moussavi, 2015). A nanocomposite made up of multiwalled-carbon nanotubes and TiO_2/SiO_2 (MWCNT–TiO_2–SiO_2) was used by Czech and Buda (2015) for the photocatalytic removal of bisphenol A (BPA) and carbamazepine (CBZ) from water solution. It was found that addition of nanocomposites (0.15–17.8 wt%) on MWCNT enhanced the removal of both these pollutants.

Ahmadi *et al.* (2017) used MWCNT/TiO_2 nanocomposite for photocatalytic degradation of tetracycline under UVC irradiation. Rate effecting operational parameters and MWCNT to TiO_2 weight ratio were studied by them. Complete removal of tetracycline was obtained at MWCNT to TiO_2 ratio (1.5 (w/w%), pH 5.0, and amount of photocatalyst (0.2 g L^{-1}).

Atropine ($C_{17}H_{23}NO_3$, Fig. 1) belongs to muscarinic antagonists group of drugs, which are competitive antagonists of acetylcholine at muscarinic receptors. Although atropine was used widely earlier in the treatment (in its sulfide form) as atropine sulfate ($C_{34}H_{48}N_2O_{10}S$, Fig. 2) for peptic ulcer but today, it is mostly used in resuscitation, anaesthesia, and ophthalmology.

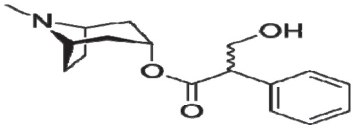

Fig. 1. Atropine

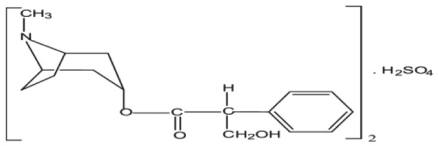

Fig. 2. Atropine sulfate

Abnormal consumption of atropine is highly toxic and can cause atropism or other side effects such as tachycardia, stupor, fever, delirium, atypical kidney function, and difficulty in swallowing. In overdoses, atropine is poisonous also. The oral minimal toxic dose (TDLo) for human is as lower as 33 µg kg^{-1}. Atropine is sometimes added to potentially addictive drugs, particularly antidiarrhea opioid drugs such as diphenoxylate or difenoxin, wherein the secretion-reducing effects of the atropine can also aid the antidiarrhea effects (Ricard *et al.*, 2012; Azizi *et al.*, 2013; Abbasifar and Samadi-Maybodi, 2016).

Experimental

Materials: Multiwalled carbon nanotubes (MWCNTs) was procured from Ad Nano Technologies Pvt. Ltd. with purity (> 99%), and average diameter (10-15 nm). Atropine sulfate (ATS) drug molecule was provided by Pacific College of Pharmacy, Pacific University, Udaipur for the present study.

Experimental: 0.0676 g of ATS (active pharmaceutical ingredient salt) was dissolved in 100.0 mL of doubly distilled water to prepare stock solution of 1.0 x 10^{-3} M. Working solutions were prepared by using this stock solution during the whole experiment for the preparation of working solutions as and when required. pH of the solutions was adjusted by pre-standardised 0.1N sodium hydroxide and 0.1N sulphuric acid. The pH of solutions was measured with a pH meter (Systronics, Model 335). The progress of adsorption was determined successively by measuring absorption by UV– Visible spectrophotometer at 230 nm at regular time intervals. Experiments were also performed to study the effect of parameters such as adsorbent dose, contact time, initial concentration, solution pH, and temperature for the removal of adsorbate on MWCNTs.

The rate constants were calculated using the conventional rate expression

$$k = 2.303 \times \text{slope} \quad \text{... (1)}$$

Removal efficiency (R) was determined by equation–

$$R\ (\%) = (C_0 - C_e) / C_0 \times 100 \quad \text{… (2)}$$

At equilibrium, amount of adsorption was evaluated by equation-

$$q_e = (C_0 - C_t)\ V / M \quad \text{…(3)}$$

Where, C_0 and C_e are the concentrations of drug at initial and equilibrium stages, respectively, C_t is concentration at time t, V (L) is the volume of the solution and W (g) is the mass of adsorbent used.

RESULTS AND DISCUSSION

Effects of Parameters

Effect of pH: Solution pH could affect the chemical speciation of MWCNTs, resulting in change of adsorption characteristics. Keeping the concentration of ATS = 5.0 x 10^{-4} M and amount of adsorbent = 0.30 g, the effect of pH in the range 5.0 to 10.5 on adsorption of ATS on MWCNTs was studied and presented in Fig. 3. It was observed that rate of adsorption increased upto pH 9.0 and then it showed declining behaviour beyond this value. A decrease in the rate of adsorption of ATS at higher pH may be due to the fact that these are present in anionic forms, which will experience a force of repulsion with the negatively charged surface of MWCNT due to absorption of more ^{-}OH ions on the surface.

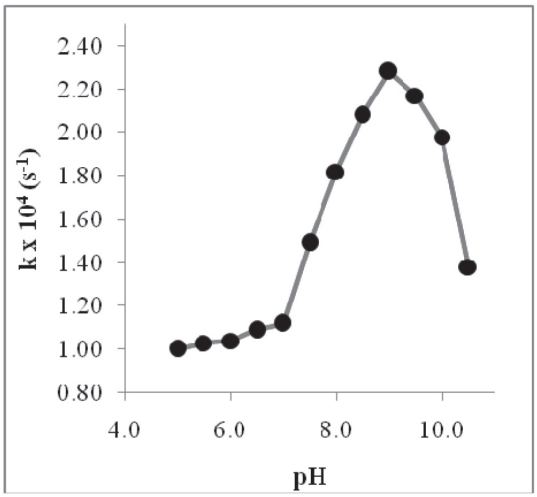

Fig. 3. Effect of pH

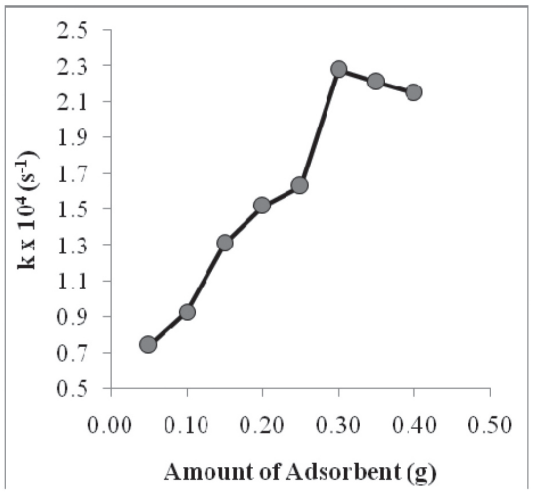

Fig. 5: Effect of adsorbent dose

Effect of concentration: The effect of concentration of drug on its removal by MWCNTs was studied keeping optimum pH = 9 and amount of adsorbent = 0.30 g. It was found to increase up to 5.0 x 10^{-4} M (Fig. 4) but after that, it was found to decrease with an increase in drug concentration. This decline in rate of adsorption may be due to increase in number of drug molecule, which will act as filter and it will not allow more drug molecule to reach to the inner space of the nanotubes.

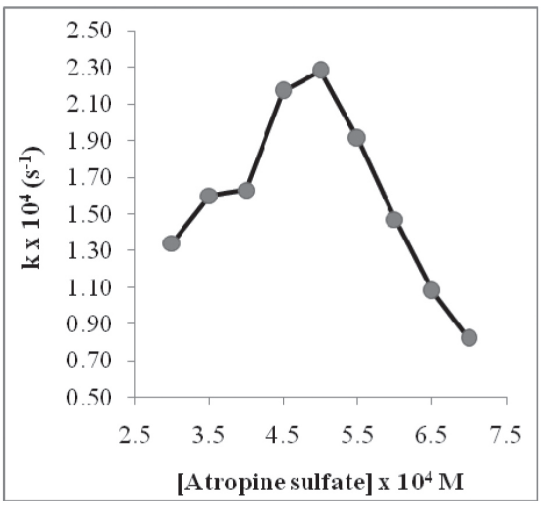

Fig. 4. Effect of drug concentration

Effect of adsorbent dose: The adsorbent dose plays an important role in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of drug solution. Fig. 5 presents the effect of variation of MWCNTs dosage on the adsorption of ATS at pH = 9, initial concentration of 5.0 x 10^{-4} M. It was observed that rate of removal of ATS increases significantly as adsorbent dose was increased upto 0.30 g of MWCNTs, but after that the rate of adsorption decreases. The increase in amount of adsorbed drug molecule with MWCNTs dosage was due to the availability of more surface area of the MWCNTs. Increasing the MWCNTs dose increases the probability of the MWCNTs entanglement in the solution, causing adsorption in the interlayer space and a decrease in the aggregation of dye at the external surface. Accordingly, the adsorption capacity declined as the MWCNTs dosage was further increased.

Contact time study: Equilibrium time is one among important parameters for wastewater treatment systems. A plot of removal efficiency of ATS onto MWCNTs with respect to contact time of 0-240 min. was studied with initial concentration of 5.0 x 10^{-4} M and 0.30 g of MWCNTs to determine and study the kinetics of adsorption (Fig. 6). It was found that at initial stage, adsorption is initially rapid (upto 90-120 min) and then it slowed down, perhaps because a large number of vacant surface sites were available for adsorption during the initial stage, and then, the remaining vacant surface sites were difficult to occupy because of the repulsive forces between the ATS molecules on the MWCNTs and the bulk phase. Due to this, the curve is single, smooth and continuous towards saturation. Maximum adsorption capacity at equilibrium was found to be 124.36 mg g^{-1}.

Evaluation of adsorption kinetics: Adsorption is a physico-chemical process that involves mass

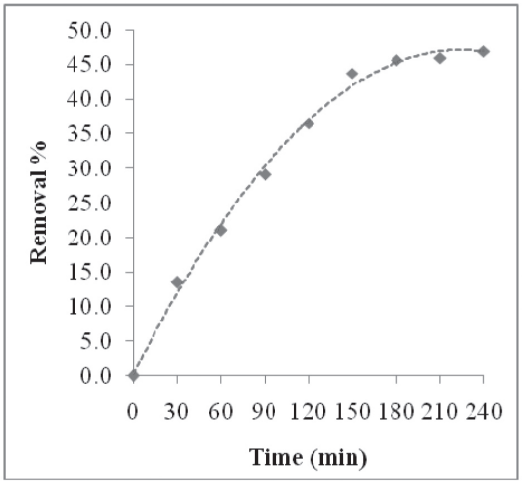

Fig. 6: Contact time study

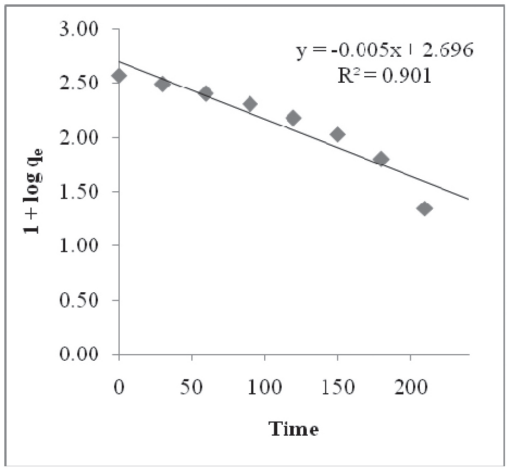

Fig. 7. Pseudo-first order plot

transfer of a solute from liquid phase to the adsorbent surface. Pseudo-first order equation and pseudo-second order equation models were used to observe the adsorption kinetic behavior of ATS onto MWCNTs. The best-fit model was selected based on the linear regression correlation coefficient values (R^2).

Pseudo–first order kinetic model can be described as -

$$\log (q_e - q_t) = \log q_e - k_1 \times t \qquad \ldots (4)$$

where, q_e and q_t are the amounts of ATS adsorbed at equilibrium and time t, respectively; k_1 is the rate constant of pseudo-first order kinetic model (s^{-1}).

The linear form of pseudo-second order is expressed as–

$$t/q_t = 1/k_2 / q_e^2 + 1/q_e \times t \qquad \ldots(5)$$

where, k_2 is pseudo-second order constant. A plot of t/q_t against t gives a linear relationship (Fig. 8). q_e and k_2 can be determined from the slope and intercept of this plot.

The value of R^2 in plots is 0.989 for pseudo-second order, which indicates that pseudo-second order model was more suitable for this adsorption process as compared to pseudo-first order model.

Intra-particle diffusion model: The kinetic experimental results were also fitted with intra-particle diffusion mechanism to gain insight to the mechanisms and rate controlling steps affecting the adsorption kinetics. The kinetic results were analyzed by the intra-particle diffusion model to elucidate the diffusion mechanism.

Intra-particle diffusion model can be described as:

$$qt = k_{id}\, t^{1/2} + C \qquad \ldots(6)$$

where, C is the intercept (mg g^{-1}), which is related to the boundary layer thickness and k_{id} is the slope, which represents the intra-particle diffusion rate constant. It can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$. If the plot of q_t versus $t^{1/2}$ is linear and passes through the origin, then intra-particle diffusion is the sole rate-limiting step.

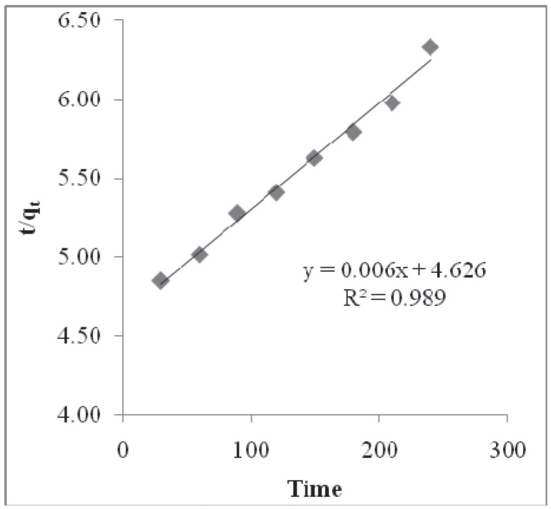

Fig. 8. Pseudo-second order plot

However, the linear plot did not pass through the origin (Fig. 9). This indicates that the intra-particle diffusion was not the only rate controlling step.

Adsorption Isotherm Study

The Langmuir and Freundlich models are the most frequently employed models. In this work, both models were used to describe the relationship between the amount of drug molecule adsorbed and

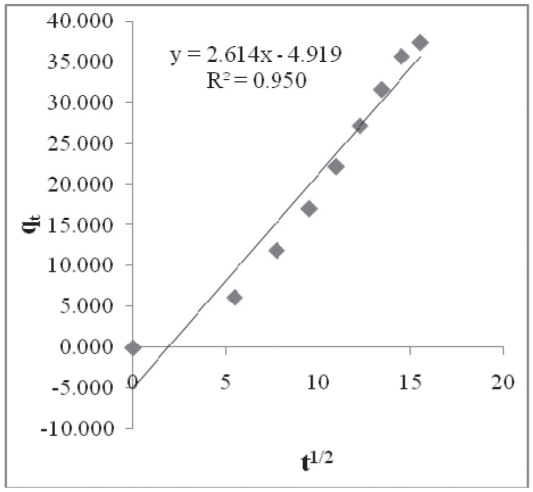

Fig. 9: Intra-particle diffusion model

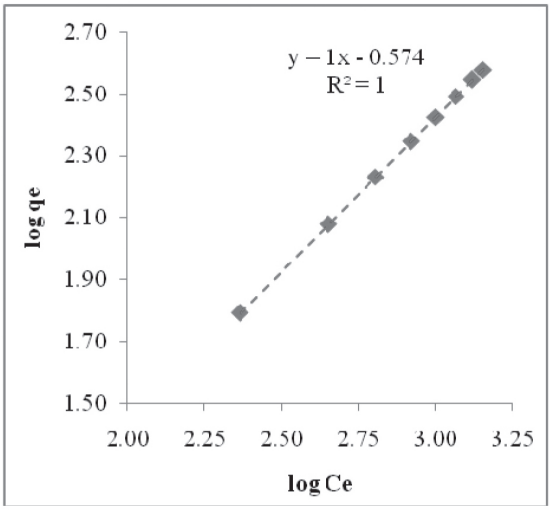

Fig. 11: Freundlich isotherm plot

its equilibrium concentration in solution.

The equation for Langmuir isotherm is-

$$1/q_e = 1/q_m \times K_L \times C_e + 1/q_m \quad \ldots(7)$$

Where, q_e is amount of dye adsorbed per unit weight of adsorbate, C_e is remaining dye concentration at equilibrium, q_m is maximum adsorption capacity and K_L is the Langmuir constant.

The Freundlich equation is based on adsorption on a heterogeneous surface and its linear form is given as:

$$\log q_e = K_f + 1/n \log C_e \quad \ldots (8)$$

Linear plots of $1/q_e$ v/s $1/C_e$ (Fig. 10) and $\log q_e$ v/s $\log C_e$ (Fig. 11) suggest the applicability of Langmuir as well as Freundlich isotherm, respectively. The R^2 value of linear correlation plot

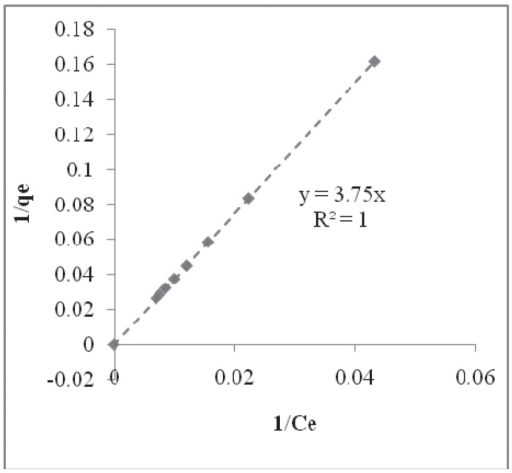

Fig. 10: Langmiur isotherm plot

of both isotherms is 1.0, which suggests that the Langmuir as well as Freundlich isotherm provides a good model for this adsorption system.

CONCLUSION

The adsorption of atropine sulfate onto MWCNTs from aqueous solutions was examined. Adsorption parameters for the Langmuir and Freundlich isotherms were evaluated and the equilibrium data were described by the both; Langmuir and Freundlich isotherm models. The adsorption kinetics can be successfully fitted to pseudo-second order kinetic model. The results of the intra-particle diffusion model suggested that this was not the only rate-controlling step. Atropine sulfate was successfully removed and maximum adsorption capacity at equilibrium was found to be 124.36 mg g^{-1}.

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