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ADSORPTION POTENTIAL OF ZnO NANOPARTICLES FOR OFLOXACIN HYDROCHLORIDE FROM AQUEOUS SOLUTIONS

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ABSTRACT

Studies pertaining to the use of nanoparticles as adsorbents have gained a lot of importance in recent years. In the present study the adsorption potential of ZnO nanoparticles for adsorption of ofloxacin hydrochloride from aqueous solution has been studied. The ZnO nanoparticles have been synthesised by precipitation method and characterized using X-Ray Diffraction, U.V and TEM. XRD data shows the particle size to be 68.61nm. Batch studies for varying drug concentration (10-100 mg/l), contact time (15-150 mins.) and pH (1-12) show that maximum removal of 79.2% takes place at pH 4 for a contact time of 120 min and drug concentration 100 mg/l, with an adsorbent dose of 100 mg/10ml. The data have been subjected to adsorption isotherm analyses using Freundlich, Langmuir, Temkin and Dubinin-Radushkevitch equations. The data fits well to all the isotherm models with high correlation coefficient values of ~0.999. Kinetic studies indicate that process follows first order kinetics and data fits to the first order rate equation. A study using the Morris Weber model shows that intraparticle diffusion occurs but is not the rate determining step.

***Keywords*: Batch Adsorption, Isotherm Analyses, Kinetics, Ofloxacin Hydrochloride, Zinc Oxide Nanoparticles.**

I INTRODUCTION

Increase in indiscriminate disposal of drug in water surface and pharmaceutical contamination in ground water system has been causing great concern due to harmful effects on environment [1]. Pharmaceuticals enter in the ground water system through pharmaceutical industries, pharmacy waste from hospitals, house hold waste and human excretion [1,2]. Antibiotics have been generally detected in the concentration range of 1-100 µg/L [3,4]. Ofloxacin hydrochloride chemical IUPAC name: (±)-9-fluoro-2, 3-dihydro -3- methyl-10- (4-methyl – 1 - piperazinyl) -7-oxo-7H - pyrido [1,2,3 de] [1,4] benzoxazine - 6 - carboxylic acid, is a commonly used broad-spectrum antibiotic agent of fluoroquinolone family[4,5]. The detected amount of these antibiotics in waste water is very minute but they are harmful for human, animal and aquatic lives even at very low concentration [6] and cause health problems like headache, diarrhea, tremors, nausea, vomiting, etc [7]. Several techniques such as

photocatalysis [8], advanced oxidation processes [9,10] and adsorption using different adsorbents e.g. clay [4] , agricultural waste [5], activated carbon [11,12], fly ash [13] and titanium oxide [14] has been reported for removal of fluoroquinolones. However, among these methods, adsorption has some advantages due to its high selectivity, high removal efficiency, ease of operation and lower cost [7]. Recently, nano metal oxides have been reported to be efficient and cost effective adsorbents for the removal of these pollutants. Nano sized particles have high effectiveness to adsorb pollutants from water because of small size and large surface area[15]. A number of methods for preparation of ZnO nanoparticles have been reported [16,17]. The ZnO nanoparticles have a large number of practical applications such as drug carrier [17], as catalyst [8] and as adsorbent for heavy metal ions e.g. Zn^{+2}, Cd^{+2}, Hg^{+2}, Co^{+2} etc [18]. However, no reports are there for the use of ZnO nanoparticles for removal of ofloxacin. In the present study, efficiency of ZnO nanoparticles as adsorbent, for the removal of ofloxacin hydrochloride from water, has been evaluated.

II MATERIALS AND METHODS

2.1 Preparation of ZnO Nanoparticles

ZnO nanoparticles have been synthesized using reported method [17]. 25 ml of 4.0 M NaOH (Merck) solution was added at an approximate rate of 5 ml/min into 25 ml of 0.2 M $ZnSO_4$ (Merck) solution diluted with 50 ml deionized water, with stirring at an ambient temperature under atmospheric conditions. The final pH of the mixture was fixed at 13 and the temperature of the mixture maintained at 60ºC, precipitation occurs after 2 h. The precipitates obtained were washed and dried at 60 ºC in an air oven. The sample of ZnO was characterized by X-ray Diffractometer (Powder Method), Panalytical.s X.Pert Pro, UV (UV-Visible 2450 spectrophotometer, shimadzu, Japan) and TEM.

2.2 Preparation of Adsorbate Solution

Ophthalmic ofloxacin hydrochloride with purity 99.8% contain 3000 mg/l of drug (Cipla) was used [19]. A stock solution of ofloxacin hydrochloride having drug concentration 300 mg/l was prepared in double distilled water. Further dilutions were carried out with double distilled water to obtain the concentration desired for the study (ranging from 10 mg/l to 100 mg/l).

2.3 Estimation of ofloxacin

Drug solution of concentration 300 mg/l was diluted to prepare the working standard solutions of concentration range 1 mg/l to 10 mg/l. U.V- visible spectrophotometer,(Shimadzu 2450, Japan) with 1 cm optical path length having quartz cells was used for all absorbance measurements [19]. Calibration curves were plotted for the estimation of drug for the pH range of 1-12 at different λ_{max} depending upon the pH under study. Linear calibration plot of ofloxacin hydrochloride for the concentration range 1mg/l to 10mg/l at pH-4 gives λ_{max} at 288.50 nm.[R] Water used as blank.

2.4 Batch Adsorption Studies

A known weight of adsorbent (100 mg) was placed in contact with 10 ml of ofloxacin hydrochloride solutions in the concentration range (100 mg/l to 10 mg/l) for regular time intervals varying from 15 mins. to 150 mins. (till attainment of equilibrium) at varying pH (1-14), adjusted by the addition of 0.1M HCl / NaOH as the case may be. The samples were subjected to agitation and the resultant solutions were centrifuged and supernatant liquids analysed for drug concentration.

III RESULTS AND DISCUSSION

3.1 Characterisation of ZnO Nanoparticles

XRD

The XRD pattern of ZnO nanoparticles shows peaks at scattering angle (2θ) of 31.7288, 34.3877, 36.2432, 47.5063, 56.5137 and 62.8756, which correspond to the reflection from (100), (002), (101), (102), (110) and (103) planes, respectively Fig. 1(a) [17]. This shows that the nanoparticles are pure zinc oxide with a hexagonal structure. The average diameter of synthesized ZnO nanoparticles was calculated using Debye-Scherrer formula [20]

$$D = 0.89\,\lambda/b\,\cos\theta \quad (1)$$

Where 0.89 is the Scherrer's constant, λ is the plane located at 36.24° and was found to be 68.61nm.

UV-Spectrum

The particle size calculated using the UV absorption spectrum of ZnO nanoparticles exhibits a strong absorption band at about 354 nm along with two small peaks at 289.50 nm and 206.50 nm which lie much below the band gap wavelength of 358 nm [17].

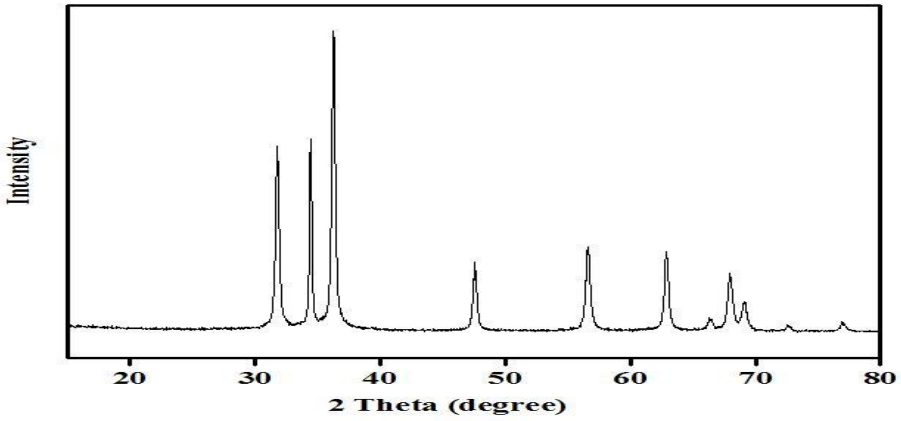

Fig. 1(a) XRD pattern of prepared ZnO nanoparticles

TEM Images

Transmission electron microscopy was performed to evaluate the particle size of ZnO nanoparticles. shows the transmission electron microscopy (TEM) image of ZnO nanoparticles. This image shows that the size of ZnO nanoparticles is very consistent. The average particle size was estimated to be 100 nm [8].

3.2 Effect of Initial Concentration and Contact Time

Fig. 2 shows that amount of drug adsorbed increases with increase in concentration, in the concentration range studied (10-100 mg/l), however, percentage removal decreases with increase in drug concentration. The increase in percentage removal with dilution is due to the availability of larger number of adsorbent sites for a smaller number of drug species for adsorption. Maximum removal takes place in the initial 15 minutes and after that increases very slowly (Fig. 2) until equilibrium is attained at 120 min. This may be explained on the basis that larger number of adsorption sites decreases with time [4,21].

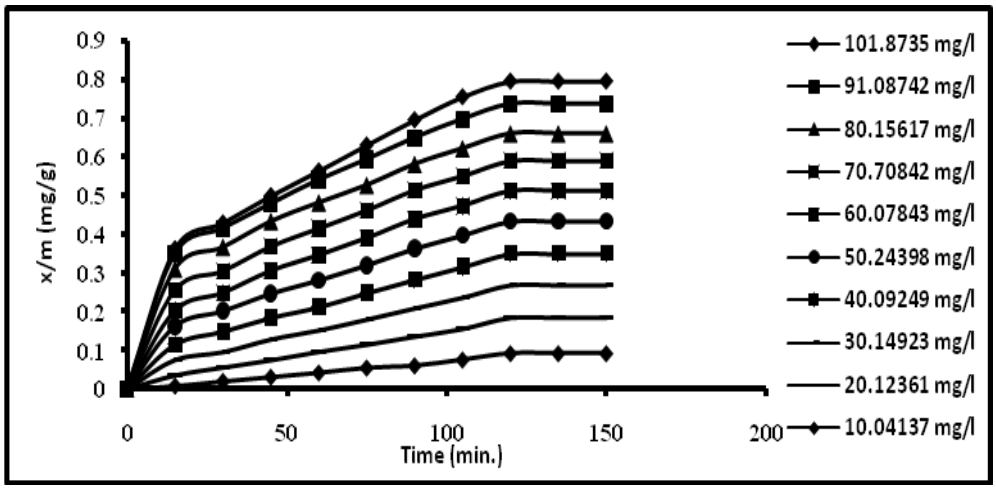

Fig. 2 Amount of ofloxacin hydrochloride adsorbed (mg g^{-1}) *vs* time (min.) at different drug concentrations at pH-4

3.3 Effect of pH

The pH of the adsorbate solution was varied in the range 1 to 12 for a contact time of 120 min. and drug concentration 100mg/l. It has been observed that removal of ofloxacin increases with increase in pH from 1 to 4 (Fig. 3) which is explained on the basis of the presence of H^+ ions which compete with cationic roup of the ofloxacin hydrochloride [4], thereafter increase in pH leads to a decrease in amount adsorbed because of competition of the drug molecules with excess hydroxide ions (OH^-) for the adsorption sites [14].

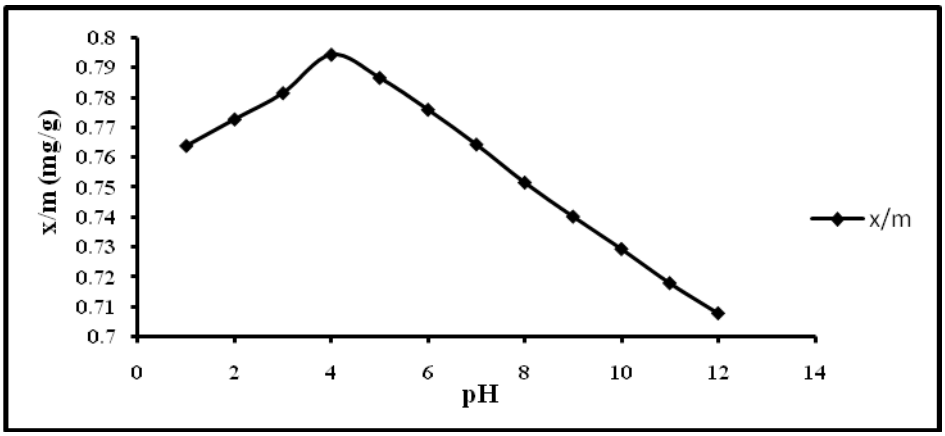

Fig. 3 Effect of pH on amount of ofloxacin hydrochloride adsorbed for a contact time of 120 minutes and drug concentration 100 mg/l

3.4 Adsorption Isotherm Modeling

The data for the removal of ofloxacin hydrochloride by ZnO nanoparticles has been analyzed at pH-4 and contact time of 120 minutes using various isotherm models

3.4.1 Freundlich isotherm

The linearised form of the Freundlich equation can be given by (2) [4]:

$$\log q_e = \log K + 1/n \log C_e \quad (2)$$

where C_e is the equilibrium concentration (mgL^{-1}) and q_e is the amount adsorbed (mgg^{-1}). The straight line plot shows that experimental data fitted well to the Freundlich isotherm model. The values of n and K, determined from slope and intercept of the linear plot are 1.0690 and 0.0111 mgg^{-1} respectively. The value of $1<n<10$ suggest the effectiveness of the adsorbent [4,22]. The applicability of Freundlich isotherm and high R^2 value of 0.999 suggests favourable and monolayer adsorption.

3.4.2 Langmuir adsorption isotherm

Langmuir equation is given by (3) [18]:

$$C_e/q_e = 1/K_L + (a_L/K_L)\, C_e \quad (3)$$

where C_e is the equilibrium solute concentration(mg/L), q_e is the amount of solute adsorbed per unit weight of adsorbent(mg/g), K_L related to affinity of the binding sites(Lmg^{-1}), a_L the Langmuir isotherm constant can be determined from a plot of C_e/q_e against C_e. A straight line obtained by plotting C_e/Q against C_e indicates the conformity of the data to the Langmuir equation[13] for the adsorption of

ofloxacin on ZnO nanoparticles. Values of constants a_L and K_L obtained from the plot are $5.43x10^2$ l/mg and 5.128.

3.4.3 Temkin isotherm

Temkin isotherm suggests that the heat of adsorption of all molecules decreases linearly with the coverage of molecules due to the repulsion in adsorbate-adsorbate molecules and the adsorption of adsorbate is uniformly distributed [5]. The Temkin equation is given by the relation…

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (5)$$

Where, q_e is the amount of solute adsorbed per unit weight of adsorbent(mg/g), $B_T = (RT)/b_T$, is constant related to heat of adsorption ($Jmol^{-1}$), T is absolute temperature (K) and R is universal gas constant, 8.314 J mol^{-1} K^{-1}. The constant b_T is Temkin isotherm constant and has been found to be 6.428 x 10^3, A_T is the equilibrium binding constant (Lg^{-1}) corresponding to maximum binding energy[5]. The values of A_T, 0.069 Lg^{-1} and B_T 0.3854 J/mol have been calculated from the straight line plot of q_e vs. ln C_e which indicating that Temkin isotherm is followed (Fig. 4).

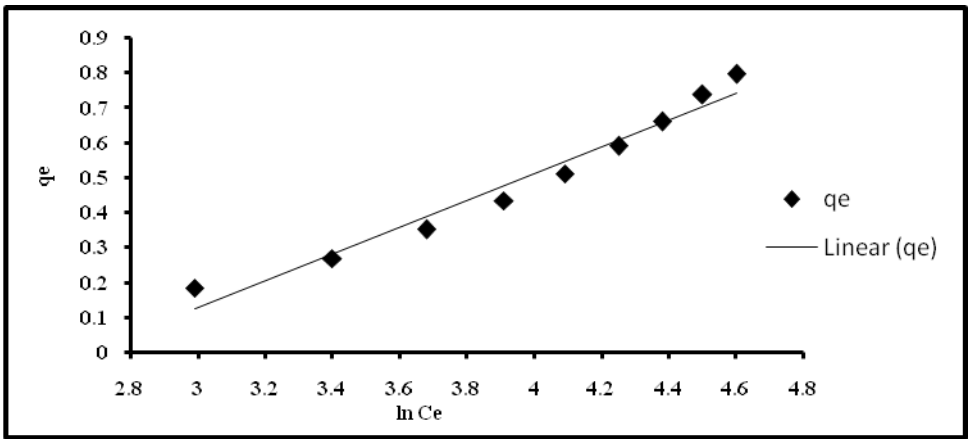

Fig. 4 Tempkin isotherm for adsorption of ofloxacin in ZnO nanoparticles at 298 K for contact time of 120 min. and pH-4

3.4.3 Dubinin-Radushkevitch (D-R) isotherm

Dubinin-Radushkevitch isotherm is represented by (6)

$$\ln q_e = \ln Q_m - K \mathcal{E}^2 \quad (6)$$

where K (mol^2 kJ^{-2}) is a constant which relates to adsorption energy, Q_m(mg g^{-1}) is the maximum adsorption capacity, The polanyi potential Ɛ , can be expressed by (7)

$$\mathcal{E} = RT \ln (1 + 1/C_e) \quad (7)$$

Where R is universal gas constant, 8.314 J $mol^{-1}K^{-1}$, T is absolute temperature (K) and C_e is the drug equilibrium concentration (mgL^{-1}). The values of D-R isotherm constants K and Q_m calculated from the plot of ln q_e and $Ɛ^2$ are found to be 0.0178 mol^2 kJ^{-2} and 0.7655 mg g^{-1} respectively. The value of mean sorption energy E (kJ mol^{-1}) is given by the relation

$$E = (K)^{-1/2} \quad (8)$$

The value of E is found to be 7.49 lies b/w 1-16 kJ mol^{-1} indicates that physical adsorption is taking place [5]

3.5 Kinetic Studies

The adsorption data obtained for ofloxacin at pH 4, concentration 100 mg/l and contact time of 120 mins. has been taken for a study of the kinetics of adsorption ofloxacin on ZnO nanoparticles. Using the basic rate equation (9) [22,23]

$$R = k\,C^{n} \quad (9)$$

Where R is the adsorption rate ($mgg^{-1}min^{-1}$), k is rate constant (min^{-1}), C is concentration (mg/L) and n is the order of reaction. A straight line plot has been obtained for log R vs. log C and the values of rate constant k and order of reaction n have been found to be 8.4 x 10^{-5} min^{-1} and 0.9595 respectively. The value of n indicates that the adsorption follows first order kinetics[23].

The results are further studied using pseudo first order rate equation

$$\log (q_e - q) = \log q_e - K_{ad}\,X\,t/\,2.303 \quad (10)$$

where q_e and q (mg g^{-1}) are the amounts of drug adsorbed at equilibrium and at any time taken for study respectively, t (min) is the time of contact and k_{ad} is the adsorption rate constant (min^{-1}). A straight line plot obtained from plot of $\log(q_e - q)$ vs. t indicates the applicability of first-order kinetics [21]. The rate constant k_{ad} (min^{-1}) and q_e (mgg^{-1}) has been found to be 0.0244 and 0.8102 respectively.

3.6 Intra-Particle Diffusion Study

The possibility of intra-particle diffusion has been studied by Morris Weber model (11), by plotting the amount adsorbed per unit weight of adsorbent (q) vs. $t^{1/2}$

$$q = K_p\,x\,t^{1/2} \quad (11)$$

where q is the amount of drug adsorbed in mg for 1g of adsorbent at different time intervals (mgg^{-1}), K_p is the intraparticle diffusion constant (mgg^{-1} min^{-1})and t is contact time (min.). K_p as calculated from the slope of the linear plot of q vs $t^{1/2}$ (Fig. 5) and has been found to be 0.491 $mgg^{-1}min^{-1}$. A straight line plot has been obtained, but does not pass through origin, that shows intraparticle diffusion occurs but is not the rate determining step [21].

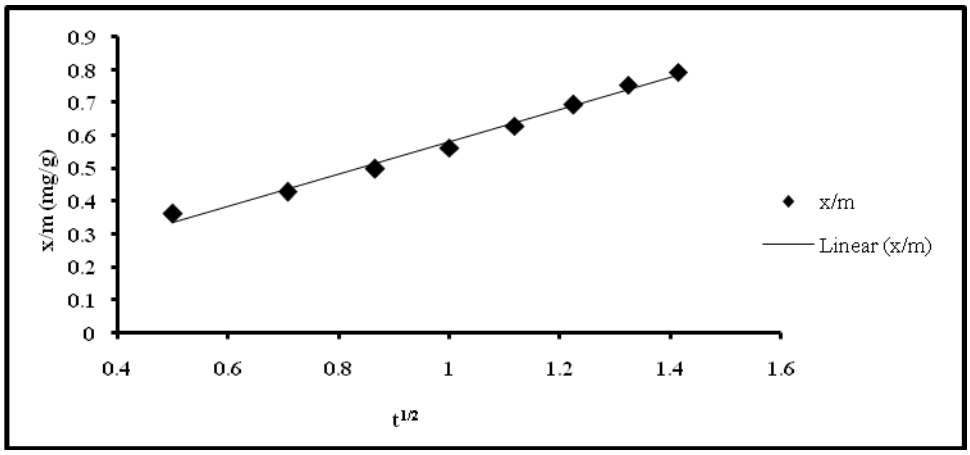

Fig.5. Plot of Intraparticle diffusion for adsorption of ofloxacin on ZnO nanoparticles at pH-4

IV CONCLUSIONS

ZnO nanoparticles were synthesised by precipitation method from zinc sulphate. XRD patterns show that ZnO nanoparticles have hexagonal unit cell structure and average particle size was found to be 68.61nm. The UV-Visible absorption spectrum shows an absorption band at 354 nm due to ZnO nanoparticles. Studies suggest that ZnO nanoparticles can be used as an effective adsorbent for the removal of ofloxacin hydrochloride from aqueous solution. The adsorption of ofloxacin hydrochloride on ZnO nanoparticles is found to be dependent on the initial drug concentration, pH and contact time. The maximum adsorption capacity was found to be 0.79434 mg/g. The removal efficiency is found to be 79.2% at pH 4, drug concentration of 100mg/l for a contact time of 120 min. (till equilibrium is attained). The experimental data fits well to all the isotherm models with high correlation coefficient values of ~0.999. The value of mean sorption energy indicates that physical adsorption is taking place Kinetic studies reveal that the process follows first order kinetics as obtained from the general rate equation and Lagergren equation. The possibility of intra-particle diffusion has been studied using Morris Weber equation and it was observed that intra-particle diffusion occurs but is not the rate determining step.

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