



Adsorptive removal of amoxicillin antibiotic from aqueous solution using Pectin-Tin(IV) molybdosilicate composite cation exchanger

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Abstract : Bio polymer based composite cation exchanger Pectin-Tin(IV) molybdosilicate was synthesized and characterized by different instrumental techniques. Cationic nature of the exchanger was confirmed by pH titration studies using NaOH/NaCl and KOH/KCl systems. The main objective of this study was to remove widely used antibiotic amoxicillin from aqueous solution using the synthesized composite exchanger. Sorption of pharmaceutical pollutant amoxicillin on to the exchanger was confirmed using UV-Vis DR spectroscopy. Kinetic models were best fitted by pseudo-second-order model with high value of R^2 compared to pseudo-first-order. Among the two isotherm used, Langmuir isotherm best fit with a maximum monolayer adsorption capacity of 119.11 mg/g. Mass transfer aspects analysed shows that sorption of amoxicillin is intraparticle diffusion controlled along with some extend of boundary layer control. Amoxicillin sorbed exchanger can be regenerated using 0.5 M NaOH as desorbing agent.

Key Words: Composite exchanger, Pectin, Amoxicillin, Waste water, Sorption kinetics.

1.Introduction

Pharmaceutical materials have recently been considered as an important class of organic pollutants because of their persistence and bioaccumulation in the environment. Among various pharmaceutical products (PPs), antibiotics are the main group used widely in medicine. Significant residues of antibiotics are directly or indirectly introduced into the aquatic and terrestrial environments due to the past and ongoing usage of large amount of antibiotics. Most antibiotics drugs are difficult to be biodegraded due to the stable naphthol ring in their structures and therefore they were targeted as pollutants of emerging concern, the development of efficient removal techniques is becoming a critical matter to be addressed¹.

Amoxicillin is a most commonly used pharmaceutical antibiotic for the treatment of various bacteria causing infections. The removal of amoxicillin from waste water is of great concern regarding the prevention of bacterial resistance and side effects of exposure. Several methods have been employed for the removal of amoxicillin from aqueous media, different treatment techniques including various sorption ², advanced oxidation process ³, membrane separation ⁴ and bioremediation ⁵ etc., were well investigated. Sorption of pollutants by ion exchangers is a dominant and efficient process for purification waste water because of its efficiency, easy handling and cost effectiveness.

Some ion exchange resins/organic ion exchangers can able to remove antibiotics from waste water significantly with an overall efficiency upto 80%⁶⁻⁸. However the problems associated with ion exchange resins

in antibiotic removal are backwashing, regeneration and appearance of fouling order and potential irreversible accumulation⁹. Also, additional problems such as low thermal and chemical stability of ion exchange resins limit their utility in antibiotic sorption technology. Composite ion exchangers can overcome this limitation by combining the advantages of both components. Composite exchangers are used widely for the removal of heavy metal inorganic pollutants and organic pollutants such as dyes and pesticides. Details of the synthesis, characterization pectin-tin(IV) molybdosilicate exchanger and its application in removal of heavy metal ions from aqueous solution had already studied¹⁰. The goal of this study is to extend the sorption ability of composite exchanger for the removal of hazardous antibiotic amoxicillin from aqueous solution and there by extending its applicability in both inorganic and pharmaceutical pollutant removal from waste water.

2. Experimental section

2.1 Reagents and chemicals

The main reagents used for the synthesis of the composite material were Stannic chloride (LobaChemie), Ammonium molybdate(E.Merck), Sodium silicate (LobaChemie) and Pectin (Lobachemie). Double distilled water was used for preparing the solutions of different concentrations. Amoxicillin was purchased from Sigma Aldrich, USA. A stock solution of 100 mg/L of amoxicillin was prepared by dissolving in distilled water and experimental solutions of desired concentrations were prepared by successive dilutions. All other reagents and chemicals used were of analytical grade.

2.2 Instrumentation

ELICO LI613 pH meter was used for pH measurements. FT-IR Spectrometer model Thermo-Nicolet Avtar 370 was used for recording IR spectra and were taken by KBr disc method, X-ray Diffractometer Bruker AXS D8 Advance for X-ray diffraction studies with Cu K α radiations, TG Perkin Elmer Diamond TG/DTA Analysis System for thermogravimetric/ derivative thermogravimetric analysis were used at a rate of 10°C in nitrogen atmosphere. Jeol Model JSM-6390LV for SEM analysis and Jeol Model-Jed-2300 was used for Energy Dispersive Spectrometric analysis. UV-Visible Spectrophotometer model JASCO V660 (Japan) was used for spectrophotometric measurements. A glass column was used for column operations. Magnetic stirrer (Remi Equipments) was used for stirring purposes.

2.3 Synthesis of Pectin-Tin(IV) molybdosilicate (Pc-SnMoSi) exchanger

Pectin-Tin(IV) molybdosilicate was prepared by simple mixing of pectin gels with inorganic precipitate of Tin(IV) molybdosilicate. Inorganic gels of SnMoSi were prepared by mixing boiling aqueous solutions of Ammonium molybdate and Sodium silicate upon vigorous stirring. pH was adjusted to acidic by adding 1.0 M HNO₃ drop wise, the gelatinous precipitate locally formed disappears upon stirring. After boiling for a few minutes, the clear solution was precipitated by addition of an aqueous solution of stannic chloride. A white gelatinous precipitate was formed. Pectin gels were prepared by dissolving varying amount (1-3 g) of pectin powders in DMW with vigorous stirring. Mixing of pectin gels with inorganic precipitate results in yellow colored gels. Constant stirring was maintained using a magnetic stirrer at room temperature (25±2°C) for 3 h. The gel obtained was left for 24 h at room temperature for digestion. The excess reagents were removed by filtration. After washing with DMW the precipitate obtained was dried convert into H⁺ form by immersing in 1.0 M HNO₃ solution with intermittent replacing of acid at an interval of 2 h.

2.4 Characterizations of the composite exchanger

2.4.1 Ion exchange capacity

The IEC of the material was determined by the column experiments and for this 1.0 g of the exchanger (H⁺ form) was packed in a glass column of 1.1cm diameter. The H⁺ ions were eluted by adding 100 mL of 1M sodium chloride solution. The effluent was collected and titrated against standard sodium hydroxide solution. The exchange capacity in meq/g was calculated using the formula(eq.1):

$$IEC = \frac{av}{w} \quad (1)$$

where 'a' is the molarity, 'v' is the volume of alkali used during titration and 'w' is the weight of the exchanger used¹¹.

2.4.2 pH titration

Topp and Pepper method¹¹ was used for pH titration using NaOH/NaCl, KOH/KCl systems. 500 mg of exchanger was equilibrated with varying amounts of metal chloride and metal hydroxide solutions. pH of each solution was measured after attainment of equilibrium and plotted against milliequivalents of OH⁻ ions.

2.4.3 Chemical stability

The chemical stability of the exchanger was assessed in mineral acids like HCl, HNO₃ and H₂SO₄, bases like NaOH and KOH and organic solvents like acetic acid, acetone, ethanol and diethyl ether. For this 500 mg of the exchanger was kept separately in 50 mL of different solvents at room temperature for 24 h. The change in colour and weight were noted.

2.5 Sorption studies of amoxicillin

Batch experimental methods are adopted for the antibiotic amoxicillin removal studies. 0.01 g of Pc-SnMoSi exchanger was added separately in 50 mL of amoxicillin solution having a concentration of 100 mg/L and was shaken on a water bath shaker for different times. Temperature of the reaction medium was kept at 30°C and pH was adjusted to 7.0. The amount of amoxicillin adsorbed was obtained by calculating the difference between the amount of amoxicillin found before and after the addition of the exchanger using Pc-SnMoSi by UV-Vis spectrophotometer at a wavelength of 271 nm. The percentage of removal of amoxicillin was calculated using the following formula(eqn.2):

$$\text{Removal \%} = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

Where, C_i is the initial amoxicillin concentration and C_e is the equilibrium amoxicillin concentration in mg/L. Kinetic parameters were evaluated using by performing the reaction in different time intervals by batch method.

2.6 Desorption and regeneration

Desorption and regeneration experiments were conducted to avoid the problem associated with disposal of the exchanger after sorption. Amoxicillin loaded exchanger was separated from the batch adsorption system by centrifugation and gently washed with distilled water. Desorption of amoxicillin was tested using 1.0 M HNO₃, 0.5 M HNO₃, 1.0 M NaOH, 0.5 M NaOH, NaCl and CH₃COONa solution as desorbing agents.

3. Results and discussions

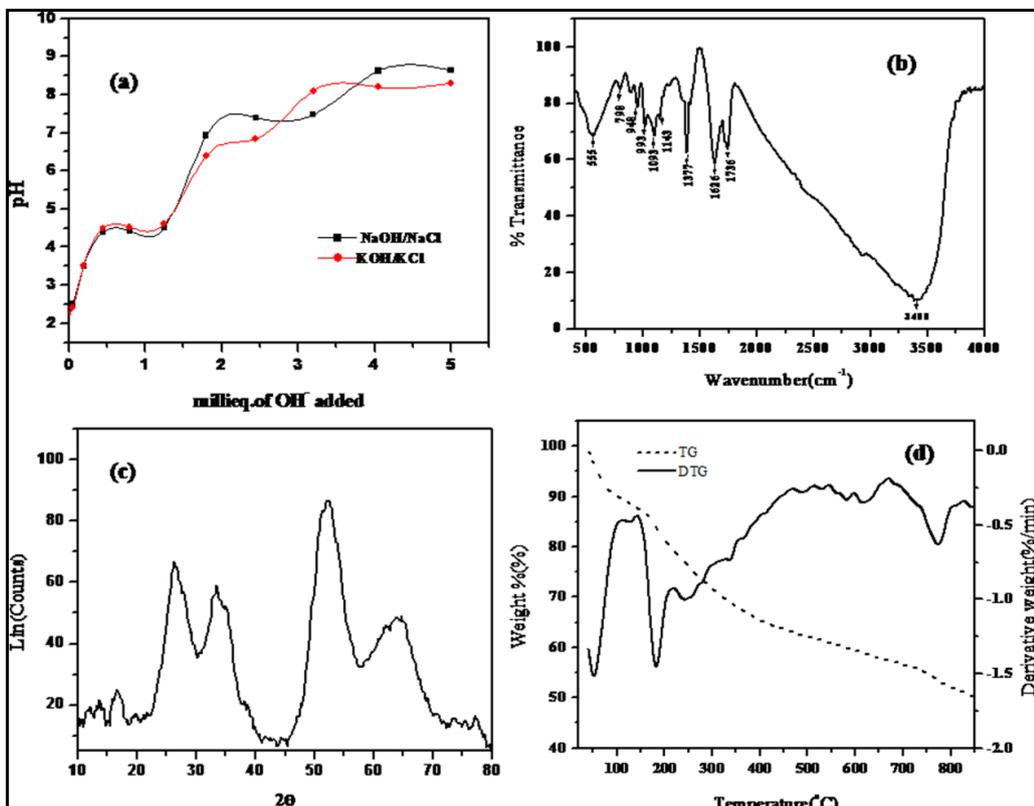
Different samples of Pc-SnMoSi composite exchanger was prepared by mixing SnMoSi inorganic precipitate and organic biopolymer pectin. **Table.1** summarizes the conditionS of synthesis and properties of biocomposite exchangers. Pc-SnMoSi-3 having mixing volume ratio of Sn:Mo:Si::1:2:1 inorganic part and 3% of pectin shows an IEC value of 1.82 meq/g and is higher than inorganic counter part SnMoSi. The sample Pc-SnMoSi was found to be quite stable in lower concentrations of mineral acids such as 1.0M HNO₃, 1.0M H₂SO₄ and 1.0M HCl, 10% solutions of bases and organic solvents such as ethanol, acetone, carbon tetrachloride etc., indicating practical applicability of the exchanger in these solvents.

Table 1 Condition for the preparations of various samples of Pc-SnMoSi composite cation exchange material

Samples	Mixing Volume Ratio				pH	Appearance	Na ⁺ IEC(meq/g)
	A	B	C	D			
SnMoSi	1	2	1	-	1	White granular	0.97
Pc-SnMoSi-1	1	2	1	1	1	Fleshy granular	1.22
Pc-SnMoSi-2	1	2	1	2	1	''	0.99
Pc-SnMoSi-3	1	2	1	3	1	''	1.82
A-0.1M SnCl ₄ .5H ₂ O in DMWB-0.1M Na ₂ Mo ₄ .2H ₂ O in DMW Na ₂ SiO ₃ .9H ₂ O in DMW							C-0.1M
D- % Of Pectin in DMW							

pH titration curve gives information about functionality behavior and nature of ionogenic group of the exchanger. **Fig.1 (a)** shows pH titration curve of Pc-SnMoSi drawn for NaOH/NaCl and KOH/KCl systems and explains more than one inflection points as indicated by sudden change in pH, infers polyfunctional nature. It appears to be strong cation exchangers as indicated by a low pH (~ 2-3) of the solution in neutral media, i.e, before the addition of NaOH to NaCl solution. The ion exchange capacity of the strong acidic groups of the composite ion exchanger determined from graph is 1.67 meq/g and is in agreement with that obtained from the column process.

FTIR spectrum of Pc-SnMoSi (**Fig.1 (b)**) shows a broad band centered at 3400 cm⁻¹ indicating the characteristics of O-H stretching vibrations. The peak present at 1097 and 1143 cm⁻¹ is assigned to C=O and C=C double bond of pectin. The band observed at 1740 was due to the presence of C=O stretching of ester. The peaks at 1377 cm⁻¹ may be due to stretching bands of free COO⁻ group in pectin¹². Also peak associated with oxides and metal hydroxides were also present below 600 cm⁻¹ region with slight shift in peak position and intensities.

**Fig.1 (a) pH titration curve, (b) FTIR, (c) XRD and (d) TG-DTG of Pc-SnMoSi exchanger**

Pc-SnMoSi shows (Fig.1 (c)) some small intense diffraction peaks centered at 26.56 °, 34.03 ° and 52.46 ° indicating weak crystalline nature of the material. The mean crystallite size estimated from the material using Debye- Scherrer method¹³ was 1.81 nm.

TG-DTG curves shows that thermal decomposition of Pc-SnMoSi(Fig.1 (d)) occurs mainly in three stages. Initial weight loss of 25% in the 50-160°C is due to moisture loss from surface and internal layer of the material. The second stage resulting in 40% loss at 200-700°C implies the degradation of biopolymer networks. Third stage of decomposition starts above 700°C due to conversion of the material into its oxide form and upto 800°C heating temperature 56% of the material was retained.

SEM images of Pc-SnMoSi shows (Fig.2(a)) fluffy smoothed appearance with some pores. Porous nature increases rate of ion exchange capacity, increases the surface area and catalytic activity of composite. EDX spectra (Fig.2(b)) indicate the presence of C, N, Sn,Mo,Si and O elements in Pc-SnMoSi without any other impurity elements. Based on the chemical composition, TGA data and IR studies, the tentative mixed oxide formula suggested for the material is $[(\text{SnO}_2)_5 \cdot (\text{H}_2\text{MoO}_4) \cdot (\text{SiO}_2)_3 \cdot (\text{C}_6\text{H}_{10}\text{O}_7)_2 \cdot n\text{H}_2\text{O}]$. The number of water molecules (n) was determined using Alberti-Torroca formula(eq.3),

$$18n = \frac{x(M + 18n)}{100} \quad (3)$$

Where x is the percentage of water content and (M+18n) is the molar mass of the material. The number of water molecules calculated was 6, includes that due to condensation of structural hydroxyl groups.

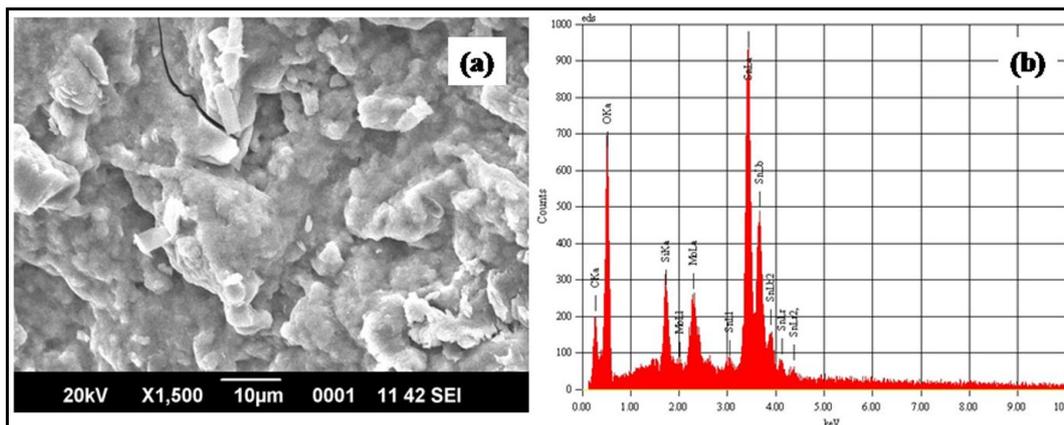


Fig.2 (a) SEM image and (b) EDX of Pc-SnMoSi exchanger

3.1 Amoxicillin loading confirmation

UV-DRS spectra(Fig.3 (a)) of amoxicillin solution taken before and after treatment with Pc-SnMoSi shows decrease in absorbance from its initial value, this indicates the sorption capability of the exchanger towards the organic pollutant amoxicillin. Also, spectrum (Fig.3 (b)) of the Pc-SnMoSi exchanger recovered after sorption of amoxicillin was entirely different from that of pure exchanger confirming that the removal process was sorption rather than degradation of amoxicillin. Amoxicillin loaded exchanger shows absorption in the entire UV and visible region of the spectrum.

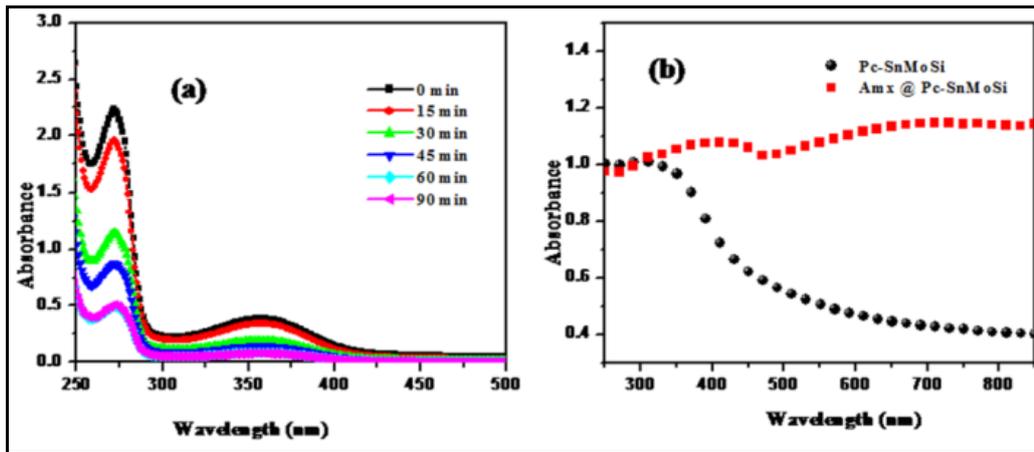


Fig.3 UV-Visible Spectra of (a) amoxicillin solution and (b) Pc-SnMoSi before and after treatment with amoxicillin

Experiments were conducted for different time intervals to determine the duration required to reach sorption equilibrium. As follows from **Fig.3 (a)**, decrease in absorbance with rise of contact time clearly indicates that amount of amoxicillin sorbed gradually increases with increase of time upto 60 minutes, after which there is no significant change in adsorption. Accordingly, 60 min is selected as the appropriate exposure time to all further experiments.

3.2 Sorption kinetics

Kinetic behavior of the exchanger towards amoxicillin was examined by monitoring the extent of adsorption with respect to contact time. Two usually applied kinetic models, pseudo-first-order model of Lagergren and pseudo-second-order model of Ho and McKay, are analysed to model the kinetic data (**eqn.4 & 5**).

Pseudo-first-order(**eqn.4**):

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (4)$$

Pseudo-second-order(**eqn.5**):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

Where q_e and q_t are the adsorption capacities at equilibrium and at time t , k_1 and k_2 are pseudo-first-order and pseudo-second-order respectively. Kinetic parameters were calculated from the corresponding plots (**Fig.4 (a) & (b)**) using linear regression analysis.

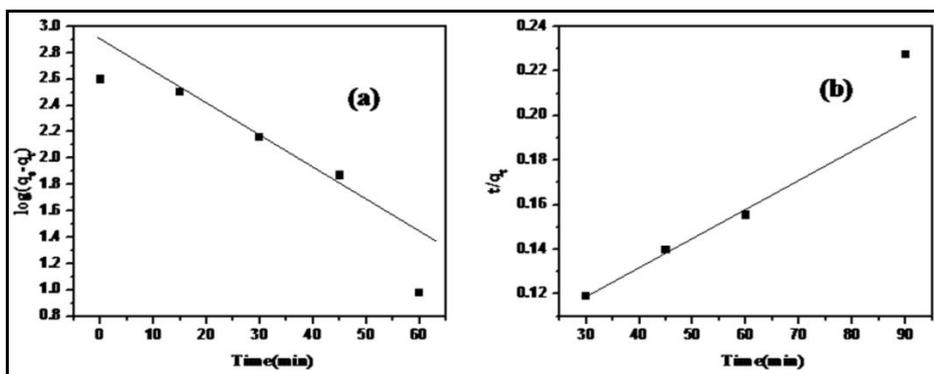


Fig.4 Linear plots of (a) pseudo-first-order and (b) pseudo-second-order kinetic models

It could be seen that experimental data were fitted by pseudo-second-order model with high value of R^2 compared to pseudo-first-order (Table.2). This indicates that the amoxicillin sorption process occurs predominantly by chemi sorption, mainly involved by valency forces through sharing or exchange of electron between the adsorbent and adsorbate.

Table. 2 Kinetic Parameters for the adsorption of amoxicillin onto Pc-SnMoSi exchanger			Table.3 Parameters for different isotherm models for the adsorption of amoxicillin ions on Pc-SnMoSi		
Pseudo-first-order			Freundlich isotherm		
q_e (mg/g)	K_1 (min ⁻¹)	R^2	K_F	n	R^2
504.2003	0.05953	0.8950	89.37	2.853	0.8634
Pseudo-second-order			Langmuir isotherm		
q_e (mg/g)	K_2 (g/mgmin)	R^2	K_L (L/mol)	q_m (mg/g)	R^2
0.5524	2.445	0.9831	2.309	190.114	0.9849

3.3 Sorption isotherm

In order to understand the mechanism of interaction between the adsorbent and adsorbate, data obtained from batch studies were fitted to different equilibrium isotherm models. In this study, two most commonly applied isotherms, Langmuir (eqn.6) and Freundlich (eqn.7) models were used.

The linearised form of Langmuir model is (eqn.6),

$$\frac{c_e}{q_e} = \frac{1}{K_L q_m} + \frac{c_e}{q_m} \quad (6)$$

The Freundlich isotherm model is expressed as (eqn.7),

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e \quad (7)$$

Equilibrium adsorption results of amoxicillin on Pc-SnMoSi exchanger were assessed based on the values of correlation coefficient (R^2) of the linear regression plot (Fig.5 (a) & (b)). In addition, the Langmuir and Freundlich parameters calculated are listed in Table. 4.

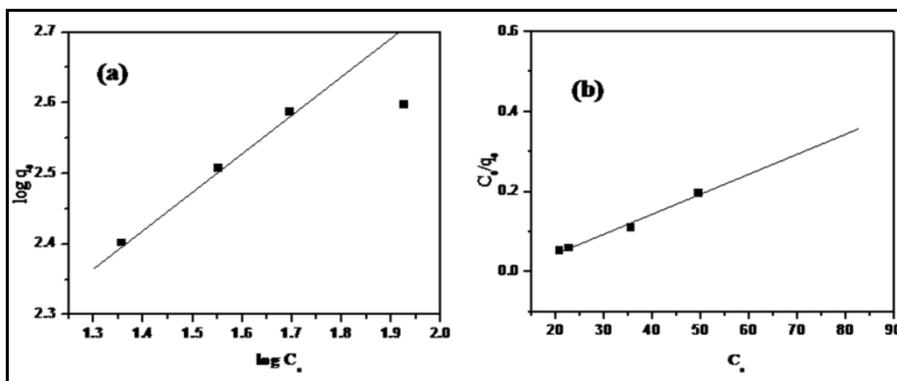


Fig.5 Linear plots of (a) Freundlich and (b) Langmuir isotherm models

The results show that the data were best fitted to Langmuir isotherm and it infers that sorption of amoxicillin is monolayer in nature. The maximum monolayer capacity of amoxicillin obtained was 190.114 mg/g. Langmuir parameters are further used to describe the affinity between amoxicillin and the exchanger using the dimensionless separation factor R_L (eqn.8).

$$R_L = \frac{1}{1 + K_L C_e} \quad (8)$$

The values of R_L indicate the shape of the isotherm to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). R_L values obtained was 0.632 suggesting favorable nature of adsorption of amoxicillin on the exchanger.

3.4 Mass transfer aspects of amoxicillin sorption on Pc-SnMoSi

In order to determine the potential rate controlling steps, mass transfer aspects of sorption of amoxicillin on the Pc-SnMoSi exchanger was analysed using intra-particle diffusion model suggested by Weber¹⁴ and its linearised form was given as (eqn.9),

$$q_t = K_d t^{1/2} + C \quad (9)$$

Where q_t is the adsorption capacities at time t , k_d is the intra-particle velocity constants and C is the constant indicating thickness of the boundary layer. A linear regression plot was drawn from the experimental data and is shown in Fig.6.

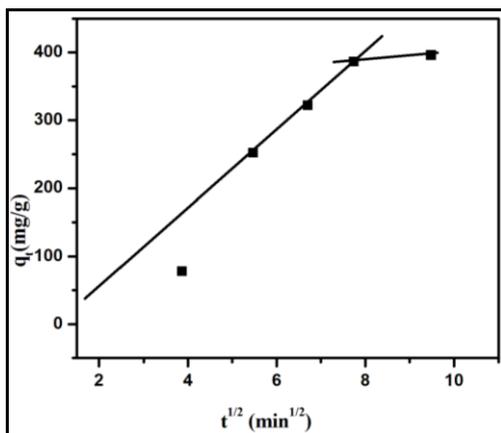


Fig.6 Intra-particle diffusion plots of amoxicillin sorption on Pc-SnMoSi

It was observed that the transportation of a solute into a solid adsorbent may be either external diffusion or film diffusion of adsorbent into the external surface or intra-particle diffusion. If the linear plots q_t Vs $t^{1/2}$ passes through origin, then it suggests that intra-particle diffusion solely determine the overall rate of the reaction. Here, it can observe that linear portion of the plots significantly deviated from origin. This divergence was due to difference in mass transfer in the initial and final stages of adsorption process. The mass transfer parameters calculated was enlisted in Table.4. The multi linearity of the plots suggests that sorption of amoxicillin on Pc-SnMoSi exchanger is intra particle diffusion controlled. Mass transfer studies suggest that in addition to the intra particle diffusion some extent of boundary layer control ($C \neq 0$) is present in the rate limiting step as indicated by significant divergence of regression lines from the origin.

Table.4 Mass transfer Parameters using intra particle diffusion model

K_d (mg/g min ^{1/2})	C	R^2
57.453	29.99	0.9456

3.5 Desorption and reusability of the exchanger

Desorption of amoxicillin was analysed using different desorbing agents such as 1.0 M HNO₃, 0.5 M HNO₃, 1.0 M NaOH, 0.5 M NaOH, NaCl and CH₃COONa solution. Desorption efficiency of 0.5 M NaOH was found to be greater. Also, in order to analyse reusability of exchanger for the antibiotic removal the adsorption-desorption cycles were repeated four times using 0.5 M NaOH as desorbing agent and the results are shown in Fig.7. A gradual decrease in sorption capacity of Pc-SnMoSi from 83.4 to 30.21 % was observed after four cycles of adsorption, which may be due to loss of some amount of exchanger in washing after every cycle. This decrease in adsorption capacity during repeated adsorption desorption cycles validate the possibility of ion exchange interactions for amoxicillin sorption.

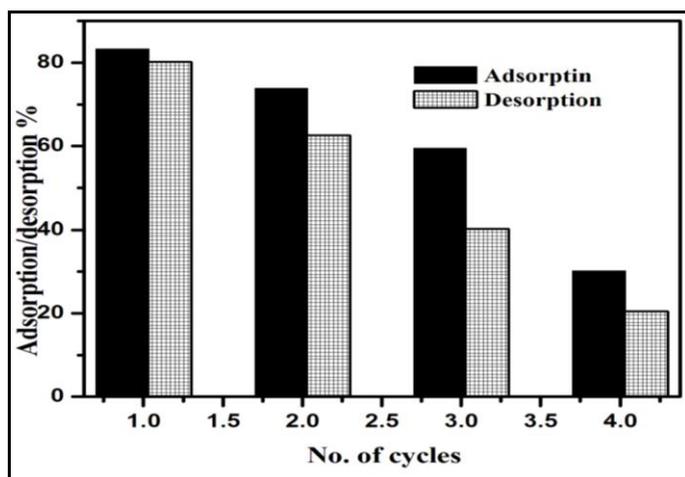


Fig.7 Reusability test of Pc-SnMoSi for amoxicillin sorption

The results in general demonstrate that Pc-SnMoSi can be used effectively for the removal of amoxicillin and the exchanger can be reused upto 4 cycles.

4. Conclusion

This study describes the potentiality of composite exchanger Pc-SnMoSi in removing toxic pharmaceutical pollutant antibiotic amoxicillin from aqueous solution. Kinetic studies on amoxicillin sorption using the exchanger follow pseudo-second-order model and isotherm study follow Langmuir model. Thus it can conclude that sorption of antibiotic was mainly chemisorption and monolayer in nature. Also mass transfer studies suggest that along with intra particle diffusion some extend of boundary layer control is also present in the rate determining step.

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