The role of combination beads for effective removal of antibiotic cefixime from water: towards of better solution

Aijaz Ahmad and Joydeep Dutta*
Department of Zoology School of Biotechnology & Biosciences, Lovely Professional University, Phagwara, Punjab, India. joydeep.dutta@lpu.co.in, Ph 9872048628
*Corresponding author

Mail id. joydeep.dutta@lpu.co.in

Abstract

Presences of antibiotics in water bodies have received widespread attention due to their potential toxicity. In this study, adsorption efficiency of synthesized beads was investigated, which were prepared by using chitosan, almond and walnut shell powder. The properties of the beads were characterized using Fourier-transform infrared spectroscopy analyses (FTIR), Scanning Electron Microscope (SEM) and energy dispersive X-ray analysis (EDX). The functioning of beads was attributed towards its antibiotic adsorption. To study the effect of dosage, pH, initial concentration and time on antibiotic adsorption, a batch adsorption experiment was conducted. Adsorption isotherms and kinetics were also studied. The adsorption isotherm experimental data is aligned with Langmuir for AWC (50% almond shell: 25% walnut shell: 25% chitosan) and CAW (50% chitosan: 25% almond shell: 25% walnut shell) beads. Whereas, WAC (50% walnut: 25% almond shell: 25% chitosan) beads follow Freundlich isotherm. The experimental data was fitted by pseudo-second order. In this study, Low initial concentration of beads was promising material for antibiotic adsorption from contaminated water.

1. Introduction

Antibiotics are widely used for the treatment of bacterial infections in humans and animals (Zhu et al., 2018; Yan et al., 2019). The estimated annual consumption of antibiotics worldwide lies between $1 \times 10^5$ and $2 \times 10^5$ tons, which are not completely metabolized by the body (Xie et al., 2019; Wang et al., 2019). Larger portion of the antibiotics (30% to 90%) subsequently get excreted through urine and feces as unmetabolized compounds (Wei et al., 2011; Xia et al., 2012; Ahmad and Dutta, 2018; Wallace et al., 2018; Wei et al., 2018). Contamination of the environment by these antibiotics are reported viz., in surface water (He et al., 2015), Ground
water (Hu et al., 2010; Ma et al., 2015), WWTP effluents (Guerra et al., 2014), sediments (Award et al., 2013), and seawater (Zhang et al., 2013). Antibiotics are regarded as “pseudo persistent” pollutant due to their sustained discharge into the water bodies and perpetual existence (Gonzalez-Pleiter et al., 2013).

These are identified as new types of pollutants in aquatic system having high biological activity, tenacious and bioaccumulative (Xie et al., 2016). When antibiotics come in contact with the environment it poses serious jeopardy for both terrestrial and aquatic organisms (Gothwal et al., 2015; Gao et al., 2015). They pose potential hazards, including acute and chronic toxicity and effect on non-target organisms (Han et al., 2016). Due to the persistent nature of antibiotics, unlike other toxins, they become detrimental to humans prompting the generation of resistant bacteria that cannot be killed easily (Wang et al., 2016; Yi et al., 2019). Bioaccumulation of these residual toxins even in minute quantities may enter the food chain that adversely affects the aquatic organisms (Xie et al., 2016). The frequently detected antibiotics and their resistant pathogens have become a worldwide problem (Van Boeckel et al., 2014; Xiao et al., 2017).

Cephalosporins (β-lactam antibiotics) are extensively used both in humans and in animals. Because of the uncontrolled use of cephalosporins, they are reported from surface and waste water systems in many countries. This has triggered a growing global concern for their potential threats to both humans and aquatic organisms as they tend to have severe and prolonged effects on ecosystems and health risks.

Adsorption is a suitable alternative for antibiotic removal from aquatic bodies as it is highly efficient, budget friendly and simple in operation. More importantly, the toxins can be meticulously removed from polluted water bodies by adsorption without leaving any risks for secondary pollution (Wang et al., 2016). Some low-cost adsorbents which have already used include sawdust date palm leaflets (El-shafey et al., 2012), paper towel (Xie et al., 2016), chitosan (Vakili et al., 2015), cellulose (Rathod et al., 2015), corn bracts (Yu et al., 2017), lotus stalk (Liu et al., 2011), rice husk (Chen et al. 2016) and walnut shell (Yu et al., 2016).

The study is an attempt to determine the cefixime adsorption behaviors onto chitosan, almond and walnut mixture beads, and also at revealing the feasibility of applying beads for cefixime adsorption from aqueous environments. This also includes the influence of initial cefixime concentration, adsorbent dosage, adsorption time and pH on adsorption efficiency.

2. Experimental
2.1 Materials
Cefixime was purchased from Yarrow Chemicals (India). Sodium hydroxide, glacial acetic acid and gluteraldehyde were purchased from Loba Chemie reagent Co. Ltd. Chitosan was purchased from Himedia. Walnut and almond shell was purchased from local market. The analytic grade reagents were used to prepare solutions.

2.2 Adsorbent preparation
Chitosan was used without further purification. Walnut and almond shells were purchased from local market and washed with distilled water to remove the dust, dried at 105 °C for 24 hrs, then grinded, sieved separately and packed in zipper packs for further use.

Chitosan, walnut and almond shell powder (in combination- AWC 50%:25%:25%, CAW 50%:25%:25%, WAC 50%:25%:25%) were dissolved in glacial acetic acid (2.0%). The solutions were agitated by a magnetic stirrer (8–10 h) at room temperature (23 ± 2°C). Then with the help of syringes the solution was released drop into a NaOH (0.5M) to form spherical beads. The beads were kept for minimum 16 h in NaOH (0.5M) for imbibition. Then the beads (1.5 gm) were treated with glutaraldehyde solution (2.5%) at pH 5 for activation. The activation process was conducted by continuous stirring (150 rpm) for 3 h. It was followed with the activated beads washing with distilled water to remove unreacted glutaraldehyde until a neutral PH is obtained and finally dried the beads in hot air oven at 50 °C for 24 hrs and stored in air tight bottles for further use.

2.3 Surface Characterization
The beads were characterized using FT-IR spectrophotometer (Shimadzu-8400) in range 4000-4500 cm⁻¹. The surface morphological structure of beads was examined by scanning electron microscope (SEM-JEOL 6100). The elemental composition of surfaces was analyzed by Energy dispersive X-ray spectroscopy (EDX).

2.4 Batch adsorption
Batch adsorption was used to study the removal efficiency of beads. The known concentration (10–50 mg/L) of cefixime in aqueous solution and mass of adsorbent (0.1 g) were kept in conical flasks. Then with the help of thermostatic shakers, all the flasks containing antibiotic solutions were agitated at 150 rpm and at 30 °C temperature. After attaining the equilibrium the adsorbent was separated and aqueous phase concentration of antibiotic was analyzed by using UV-
spectrophotometer. The adsorption parameters such initial concentration (10-50 mg/l), pH (3-11), reaction time (30-180 min) and adsorbent dosage (0.1-1 gm) were evaluated. The removal efficiency and the adsorption capacity of cefixime by prepared beads are calculated according to the equations as follows (Kumar et al., 2018):

\[
\% \text{ removal} = \frac{C_0 - C_e}{C_e} \times 100
\]

\(C_0\) (mg/L) is the initial and \(C_e\) (mg/L) equilibrium concentration of the target contaminant, respectively.

3. Results and discussion

3.1 Surface characterization studies

The spectrogram for the beads was taken within the range of 450-4000 cm\(^{-1}\), which was performed to detect functional groups present on the adsorbent who can potentially favor the adsorption of antibiotics. As depicted in Fig. 1 OH, N-H and CO groups are identified on the prepared beads as a good choice for adsorption process (Kumar et al., 2018). The first bands between 3700-3800 cm\(^{-1}\) attributes to the stretching vibration of C-H bond suggesting either presence of alkenes or aromatic compounds in AWC (a) and CAW (b) beads. The peaks at 3273 cm\(^{-1}\), 3255 cm\(^{-1}\) and 3327 cm\(^{-1}\) in ACW CAW and WAC (c) beads indicate Hydrogen bonding O-H stretch suggesting the presence of phenols and alcohols. The sharp peaks at 2359 cm\(^{-1}\), 2362 cm\(^{-1}\) and 2359 cm\(^{-1}\) confirm a presence of N-H group for amines. When reaction occurs between aldehyde groups of glutaraldehyde and some amino groups of beads, the amine groups might be formed. The transformation is supported by the presence of peaks at 1643 cm\(^{-1}\), 1647 cm\(^{-1}\) and 1583 cm\(^{-1}\), highlights a C=O stretch suggestive of alkenes.

![Fig.1 FTIR images of AWC (a), CAW (b) and WAC (c) beads.](image-url)
Scanning electron micrographs presents the morphology of synthesized beads. The pre-processed AWC (Fig. 2a) beads SEM image show topographical features of being irregular to wavy in appearance. The surface shows different gradients of density along with presence of sparsely scattered fissures and occasional pores. The images of beads after adsorption (Fig. 2b) still appears to be multiple layered but individually aggregates present more of an even surface topography and resembling clouds of an overcast sky. In case of CAW (Fig. 2c) beads SEM image shows surface topography to be multiple layered and uneven along with formation of chunks of varying sizes fissures and conspicuous pores can be also seen selectively. The post processed image (Fig. 2d) shows that the agglomerates previously formed have mellowed down in terms of size and adhesion pattern thereby clearly indicating an activity. The WAC bead (Fig. 2e) surface seems rough, multiple layered, scattered in patterns of being sparse, discrete to be assorted somewhere thus giving an uneven outlook. The post processed SEM image (Fig. 2f) after adsorption shows, agglomerates have become more condensed, tightly packed thereby look more coerced, though the surface seems to be still rough, multiple layered but overall seems to be more fortified. Fig. 2 (a, b, c) signifies the EDX spectra of ACW, CAW and WAC beads. The elemental composition of beads is mentioned on graphs and the beads contain carbon component followed with oxygen.
Fig. 3 EDX images of AWC (a), CAW (b) and WAC (c) beads.

1.2 Effect of adsorbent dosage

Fig. 4 represents the antibiotics uptake by prepared beads at different adsorbent doses. The percentage removal increased from 76 to 89 % on AWC beads, 79 to 88% on CAW beads and 79 to 90% on WAC beads, when the amount of adsorbents were increased from 0.1 to 1gm. the percentage of removal increased slightly with increased dosage of adsorbents. The results obtained can be explained by the fact that by raising the dosage of adsorbents to the correct quantity, the active sites of the adsorbent surface will increase and more antibiotic molecules can be adsorbed on the surface of the beads (Ahsan et al., 2018).

Fig. 4 Adsorption efficiencies on AWC, CAW and WAC beads of cefixime at different adsorbent dosage (V = 50 ml, ini. Con. = 30 mg/l, shaking speed 150 rpm and temperature ± 25± 1 °C).

3.3 Effect of contact time

Different time intervals (30 to 180 min) were used to understand the removal efficiency of cefixime. The removal of cefixime antibiotic was observed to be increasing initially (Fig. 5). The equilibrium exposure time for CAW and AWC beads (120 min) were observed to exhibit maximum adsorption of 77 % respectively. In case of WAC beads adsorption equilibrium was
attained at 90 min with adsorption of 80% of cefixime. WAC beads removed 71.01% cefixime after 30 mins and 84% at 180 mins. Thus, it shows 18.31 % removal efficiency from the start of experimental time period. Whereas, AWC and CAW beads showed 32.75 % removal of cefixime from the start to end (30-180) of the experiment. In the beginning, the percentage removal of cefixime was rapid due to the larger surface area of an adsorbent available, but it slowly decreased over time until it reached equilibrium. It is mainly due to active site saturation which does not permit further adsorption (Azarpira and Balarak, 2016).

3.4 Effect of pH on adsorption

In general, pH plays an important role in controlling the entire adsorption process (Ahsan et al., 2018). The effect of pH (3-11) on the adsorption of cefixime on combination beads was studied. The maximum cefixime removal was observed at 7 in case of AWC (79%) and CAW (81) beads, whereas the maximum adsorption on WAC (82%) beads was observed at pH 5.0 (Fig.6). Further increase in pH causes decrease in adsorption percentage for all the three different combinations. The pH of solution is a significant factor which affects the adsorption of cefixime antibiotic, as it can influence surface charges of the adsorbent and the structure of antibiotic molecules (Yadav et al., 2018).
3.5 Initial concentration of cefixime on its removal

The adsorption study was done by using different concentrations of the cefixime (10 to 50 mg/L) while keeping all other conditions constant in order to check the effect of the initial concentration of the antibiotic on adsorption. The adsorption decrease rapidly with the increase in initial concentration of cefixime antibiotic (Fig. 7). The adsorption decrease with the increase in concentration from 93 to 60% in case of AWC and WAC beads and 94 to 65% in case of CAW beads. The reason being, the vacant adsorption active sites remain the same but the number of antibiotic molecules increases with increase in the initial antibiotic concentration (Balarak et al., 2016).

3.6 Adsorption isotherm

Adsorption isotherms is used to elucidate the relationship between remaining residual concentration of adsorbate in the system and adsorbate adsorbed on adsorbent at equilibrium.
(Ce) (Kumar et al., 2018). The mechanism of adsorption is explained by using a number of isotherm models. The data was fitted with Freundlich and Langmuir models (Pal et al., 2017). According to Langmuir isotherm, the adsorption occurs as monolayer form on a homogenous surface (Singh et al., 2016).

Langmuir equation:

\[
\frac{1}{Q_e} = \frac{1}{Q} + \frac{1}{bQ_c}\]

where Q (mg g\(^{-1}\)) and Ce (mg L\(^{-1}\)) are maximum adsorption and equilibrium concentration of antibiotic. qe (mg g\(^{-1}\)) antibiotic adsorbed per unit weight of the beads at equilibrium and b (L mg\(^{-1}\)) is the Langmuir constant for affinity to the binding sites. The plot between Ce/qe and Ce is shown in Fig 8 (a).

Freundlich model states the uptake of adsorbate occurring on a heterogeneous surface (Sutirman et al., 2018) which is represented by the linear as below;

\[
\log Q_e = \log K_f + \frac{1}{n} \log Ce
\]

K\(_f\) represents Freundlich constant, n is the heterogeneity factor of the volume (Fig. 8b). The regression equations parameters are summarized in Table 1. The experimental data fitted best with Langmuir model for AWC and CAW beads and Freundlich model for WAC beads.

![Fig. 8. Adsorption isotherms of (a) Langmuir model (b) Freundlich model.](image)

| Langmuir isotherm | AWC   | CAW   | WAC   | Freundlich isotherm | AWC   | CAW   | WAC   |
|-------------------|-------|-------|-------|----------------------|-------|-------|-------|
| Q (mg/g)          | 17.409| 17.182| 18.179| k\(_f\) (mg/g)       | 6.173 | 5.531 | 4.946 |
| b (L/mg)          | 0.354 | 0.464 | 0.438 | 1/n                  | 0.338 | 0.407 | 0.552 |
| R\(^2\)           | 0.989 | 0.989 | 0.943 | R\(^2\)              | 0.975 | 0.908 | 0.980 |
| SD                | 0.0030| 0.0028| 0.0070| SD                   | 0.016 | 0.037 | 0.020 |

Table 1. Various constants related to adsorption isotherms.
3.7 Adsorption kinetics

The Lagergren Pseudo first order and second order kinetic models were used to evaluate the kinetics of the adsorption, which helps in estimating the mechanism and nature of adsorption.

Lagerngren pseudo-first order equation: \[ \log (Q_e - Q_t) = \log Q_e - \frac{K_1 t}{2.303} \]

Lagerngren pseudo-second order equation: \[ \frac{t}{Q_t} = \frac{1}{h} + \frac{t}{Q_2} \]

Qe and Qt (mg/g) is the antibiotic adsorbed at equilibrium and at time t (min.). \( k_1 \) (min.\(^{-1}\)) represents Lagerngren pseudo first order rate constant and \( h = k_2 Q_2^2 e \) and \( k_2 \) (in mg/g/min) denotes Lagerngren pseudo second order rate constant (Kumar et al., 2018). The graphical representation of models is shown in Fig. 9. (a-b). The constants \( k_1, Q_e \) and \( R^2 \) of cefixime removal were calculated from these plots (Table 2). Initially, large concentration difference occurs between the aqueous and the adsorbent surface which is accountable for a quicker adherence of solute onto the adsorbent surface. However, after a certain period, slow intraparticle diffusion occurs at the internal adsorption sites of the adsorbent (Kumar et al., 2018). It is evident from Table 2 that, on the basis of \( R^2 \) values, adsorption on all types of beads follows Lagerngren pseudo second order kinetic model.

![Fig. 9 (a) pseudo first order kinetic model (b) pseudo second order kinetic model.](image)

Table 2. Comparison of various kinetic models.

|                | Pseudo-first-order constants | Pseudo-second-order constants |
|----------------|-------------------------------|-------------------------------|
|                | AWC  CAW  WAC                 | AWC  CAW  WAC                 |
|                |                               |                               |
4. Conclusion

The idea of the present study gets initialized by combining powder of chitosan, walnut and almond shell to form beads. The FTIR data suggested the presence of N-H, OH and CO groups on beads, favors adsorption. The SEM image shows surface topography to be multiple layered, scattered in patterns, rough and uneven along with formation of chunks of varying sizes fissures and conspicuous pores can be also seen selectively. Optimum contact time for equilibrium attainment for AWC and CAW beads were found to be 120 min, and for WAC beads was 90 min. The maximum adsorption efficiency (% removal) was achieved at pH 5.0 in case of WAC beads and at pH 7.0 maximum adsorption efficiency was observed on AWC and CAW beads. Lagergren Pseudo second order model provide best fit in case of all types of beads. The experimental data fitted well to the Langmuir adsorption isotherm in case of AWC beads and Freundlich isotherm in case of CAW and WAC beads. The adsorption of cefixime onto WAC beads shows better results as compared to other two combinations for all the different parameters taken in the study. However as the concentration of drug is increased the beads could not able to remove the drug efficiently. Overall the result of the study states that the combination beads are efficient adsorbent for the removal of cefixime existing in effluents.

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