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Activated carbon-polyethyleneimine-alginate composite fiber for scavenging pharmaceuticals with different charges from aqueous solutions

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Abstract Activated carbon (AC) is a potential adsorbent for water purification, though it is difficult to separate after use. To solve this problem, for the first time, the ternary composite fiber (ACPEIA) of AC, polyethyleneimine (PEI), and alginate (A) was fabricated as a multifunctional adsorbent for scavenging pharmaceuticals with different charges from the aqueous environment. The hydroxyl functional group of AC was bonded with the aldehyde group of glutaraldehyde through nucleophilic addition resulting in adduct containing free aldehyde moiety for the action of cross-linker. The aldehyde functionalized AC was crosslinked with the amino group of PEI and the hydroxyl group of A resulting in ACPEIA. The carboxyl group of ACPEIA was further crosslinked with calcium ion through ionotropic gelation to give a stable fiber. The fiber demonstrated as a scavenger for removal of model contaminants with different charges such as 1-naphthol (NPT) as neutral, diclofenac (DCF) as anionic, and amitriptyline (AMT) as cationic pharmaceuticals at pH 6.5. The fiber revealed a maximum adsorption capacity of 814 μmol g^{-1} for NPT, 450 μmol g^{-1} for DCF, and 410 μmol g^{-1} for AMT. FTIR and XPS spectra of the fiber before and after sorption supported the adsorption mechanism like electrostatic interaction.

Keywords: Activated carbon, Polyethyleneimine, Alginate, Pharmaceuticals, Adsorption

1. Introduction

pharmaceuticals are consumed while treating diseases of humans and animals, but the undigested portion released into the environment contaminates water (Rakić et al., 2015). Although the very low concentration (ng L−1 to μg L−1) of the pharmaceuticals is detected in the water, they can cause serious water pollution owing to continuous addition in the water, nonbiodegradable nature, and combinatory effect based on synergistic effect (Luján-Facundo et al., 2019). Diclofenac as an arylacetic acid non-steroidal anti-inflammatory drug (NSAID), amitriptyline as a tricyclic antidepressants and 1-naphthol as a precursor of drugs are manufactured and used for medication (Hasan et al., 2016; Tsai et al., 2016). In contrast, the drugs have been detected in the sea, lakes, and rivers due to the low removal efficiency of the wastewater treatment plant. Therefore, an effective method is essential to mitigate the inefficiency problem of the plant. Among the existing pharmaceutical removal technology, adsorption based on adsorbents is regarded as an effective method. Different adsorbents like porous carbon (AC, GO, MWCNT, SWCNT, charcoal, biochar), biopolymers, synthetic materials and natural zeolites have been used to remove the pollutants (Baccar et al., 2012). However, they do not have enough adsorption capacity, kinetics, chemical stability, recyclability, and separability. Therefore, multifunctional scavenger composite adsorbents to solve the problems, are still needed for pharmaceutical removal.

AC is a widely applied adsorbent for water treatment owing to pore structure, surface functionality, high surface area, and hydrophilicity(Liu et al., 2010; Prajapati et al., 2016). However, direct use of it as an adsorbent has a separation problem making the process costly and complicated. Numerous efforts have been done to solve this problem either directly making it into different shapes like fiber, granules, and membranes or compositing it with biopolymers. For example, activated carbon fiber showed good adsorption performance for pharmaceuticals removal (Zhao et al., 2020). Carbon cloth also demonstrated excellent removal capacity for organic contaminants (Masson et al., 2016). A binary composite of AC and alginate beads could remove 98 % naproxen (Ozcan and Saloglu, 2020). However, very few composites constituted cationic, anionic, and aromatic binding sites, as adsorbents have been designed to scavenge ionic and neutral pharmaceuticals from neutral solutions.

In this study, to address above mentioned challenges, for the first time, ternary composite fibers of anionic alginate with aromatic activated carbon and cationic polyethyleneimine were blended through a facile approach for scavenging pharmaceuticals. Aldehyde functionalization of AC was carried out first with GA to permanently fix the alginate and PEI into it. The fibers were applied for scavenging cationic (AMT), anionic (DCF), and neutral (NPT) pharmaceuticals from neutral

solution. The adsorption isotherm and kinetics were studied to evaluate the pharmaceutical's adsorption performances with composite fiber. Moreover, the fibers were characterized before and after sorption of model pharmaceuticals with Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS).

2. Materials and methods

2.1. Materials

All analytical grade chemicals obtained from Sigma-Aldrich were used during the experiment. 1-Naphthol, Diclofenac and Amitriptyline were selected as model pharmaceuticals. 2 % (w/v) Calcium chloride solution and 0.1 % Glutaraldehyde (GA) solution were prepared in deionized distilled water (DW). AC, PEI, and sodium alginate solutions were prepared on the spot. Acetonitrile of HPLC grade and sodium dihydrogen phosphate solution were used in HPLC.

2.2. Preparation of Alg:AC:PEI composite fiber

PEI solution was prepared by dissolving 1 g PEI in 90 mL DW under magnetic stirring for about 30 minute.1 g of alginate was added to the stirring solution of PEI and continued magnetic stirring for 4h. After 10 min magnetic stirring of 100 µL of 0.1% GA solution in 10 mL DW, 2g powder AC obtained by grinding granular AC was added to GA solution under stirring. After 3h, GA/AC mixture was transferred to Alg/PEI mixture and continued stirring for 24 h. About 10 ml of the mixture was forced through the nozzle into 500 mL of 2 % $CaCl_2$ solution to get fibers. After then, fibers were washed with DW and freeze-dried for 24h to get Alg-AC-PEI (1:1:1) fibers. Different ratio fibers were prepared by following the above procedure except by taking different amount of AC and PEI. Three types of fibers namely (a) Alg-AC-PEI (1:1:1), (b) Alg-AC-PEI (1:2:1), and (c) Alg-AC-PEI (1:1:2) were prepared to observe the effect of PEI and AC on the sorption of pharmaceuticals.

2.3. Sorption experiment

Prepared 1000 µmol/L stock solution of each 1-naphthol, diclofenac, and amitriptyline were diluted to get the required concentration for the sorption experiment. The composite Alg-AC-PEI (1:2:1) fibers (0.01g) were added in 0.03L of pharmaceuticals. The pH of the solution was adjusted by adding drops of HCl or NaOH. The sample mixtures were shaken at room temperature under 120 rpm for the required time period. The concentration of pharmaceuticals was determined with HPLC. The pharmaceuticals equilibrium sorption capacity [q_e (µmol/g)] and % adsorption onto fiber were determined according to equation (1) and (2):

$$q_e = \frac{(C_o - C_e)V}{M} \quad (1)$$

$$Adsorption\ precentage\ (\%) = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (2)$$

Where,C_0 being initial and C_e being equilibrium pharmaceutical concentrations (µmol/L), V is the volume (L), M is the mass of adsorbent (g).

3. Results and discussion

3.1. Characterization and mechanism interpretation

FTIR and XPS of ACPEIA constituents were done to verify aldehyde functionalization of AC and the pharmaceuticals adsorption mechanism. As shown in fig.1cI and II, in FTIR spectra, the peak of the hydroxyl group in AC-GA is clearly reduced in comparison to that of AC owing to the formation of acetal or hemiacetal. Also, alkoxy group intensity in AC-GA is relatively increased compared to AC due to the presence of it in acetal or hemiacetal product of crosslinking. This supports the linking of AC with GA. As shown in fig.1a and b, the three different positions of deconvoluted XPS spectra of C 1s at 284.78, 285.68, and 289.28 eV represents C-C, C-O-C, and C=O species respectively. The changes in O/C ratio (calculated from atomic concentration) from 0.13 of AC to 0.12 of AC-GA proved the cross-linking of AC with GA. The enhanced molar ratio (calculated from peak area) of C=O to C-C, from 0.21 of AC to 0.27 of AC-GA, verified the presence of the free aldehyde group. Theoretically, bonding of GA with AC through acetal or hemiacetal bond results decrease in the molar ratio of C=O to C-C due to the absence of free aldehyde maoity or presence of more C-C in AC-GA (Hua et al., 2017). However, the enhanced carbonyl molar ratio from the XPS result showed the probability of GA being grafted on AC via one maoity. Consequently, the molar ratio of C=O to C-C increases in contrary to the theory.

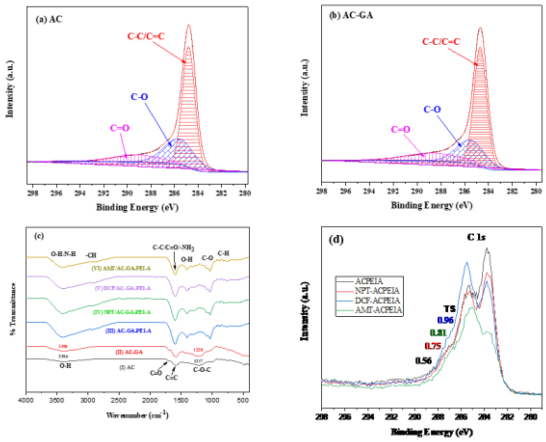

Figure 1. (a) C 1s XPS spectra of AC, (b) C 1s XPS spectra of AC-GA, (c) FTIR spectra, and (d) C 1s XPS spectra

As shown in fig.1CIII, IV, V, and VI, in FTIR spectra, the O-H and N-H bond stretching vibration of the composite fiber at 3396 changes to 3398 after adsorption of NPT, 3396 after adsorption of DCF, and 3400 after adsorption of AMT. The change in peak value pointed out the interaction between adsorbate and adsorbent through hydrogen bonding. The broad peak indicates the presence of a large number of hydroxyl and primary amino groups in the composite which reduces after adsorption due to participation of them in a hydrogen bond (Terzyk, 2001). The C=O of carboxylate salt in alginate, aromatic C=C of AC, and N-H of PEI show absorption peak at 1601 cm^{-1} which decrease to 1598, 1597, and 1596 cm^{-1} after sorption of NPT, DCF, and AMT. Such decrease in absorption peak value implies (I)

π-π, (II) ionic, and (III) hydrogen bond interaction between adsorbate and adsorbent. The peak at 1409 due to carboxylic acid O-H and alcoholic O-H bending of the fiber shifts to 1404, 1405, 1404 after sorption of the pharmaceuticals. It emphasizes hydrogen bonding between the O-H functional group of fiber and O-H/N-H functional group of target pharma. The stretching vibration of primary alcohol C-O and aliphatic C-N present in fiber occurs at 1035 cm^{-1} and decline to 1033, 1034, and 1033 cm^{-1} after sorption of adsorbate depicting participation of them in hydrogen bonding. The aromatic C-H bending at 885 cm^{-1} of fiber is mainly due to AC, which changes to 879, 892 758 cm^{-1} after sorption indicating the change in the electronic environment with electron cloud overlap. Furthermore, the peak at 2900 cm^{-1} belongs to aliphatic C-H stretching and bending vibration which reduces after adsorption pointing adsorption of adsorbate onto the adsorbent.

The changes in C 1s XPS spectra of the fiber before and after NPT, DCF, and AMT adsorption as shown in Fig 1d support the pharmaceuticals adsorption. Furthermore, the increment in TS value (C2/C1 intensity ratio) of NPT-ACPEIA (TS=0.75), DCF-ACPEIA (TS=0.96) and AMT-ACPEIA (TS=0.81) compared to ACPEIA (TS=0.56) pointed out π-π interaction as well as the higher affinity of DCF toward the fiber than AMT and NPT.

3.1. Kinetics and Isotherms

The sorption kinetics of Alg:AC: PEI (1:2:1) composite fiber was investigated by mixing 0.05g adsorbent dose with 150mL of 100µmol/L pharmaceuticals under different contact times. The kinetic experiment was done to observe the sorption mechanism and rate of sorption. The experimental kinetic data were fitted with pseudo-first-order and pseudo-second-order kinetic model (Antunes et al., 2012). The fittings are shown in the following equations:

Pseudo-first-order

$$q_t = q_e(1 - e^{-k_1 t}) \quad (3)$$

Pseudo-second-order:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (4)$$

Where, q_e and q_t (µmol/g) are the pharmaceuticals sorption capacity at equilibrium and t time (h), t is contact time (h), k_1 and k_2 (g $µmol^{-1}$ h^{-1}) are the kinetics rate constants for pseudo-first-order and pseudo-second-order.

Fig.2a and b, demonstrate kinetic curves and table 1 shows kinetic parameters for sorption of 1-NPT, DCF, and AMT. The rate of model pharmaceuticals sorption with fiber is very fast within 1 h owing to the available sorption site. The equilibrium state is attained after 8 h in the case of NPT and DCF whereas it is after 10 h in the case of AMT indicating saturation of active site. The higher correlation coefficient (R^2) values of NPT, DCF, and AMT fitted with pseudo-second-order model than pseudo-first-order model depicted chemisorption process. The fitting parameters reveal that the experimental data are well fitted by pseudo-second-order model than pseudo-first-order model. The experimental q_e value is near with calculated value.

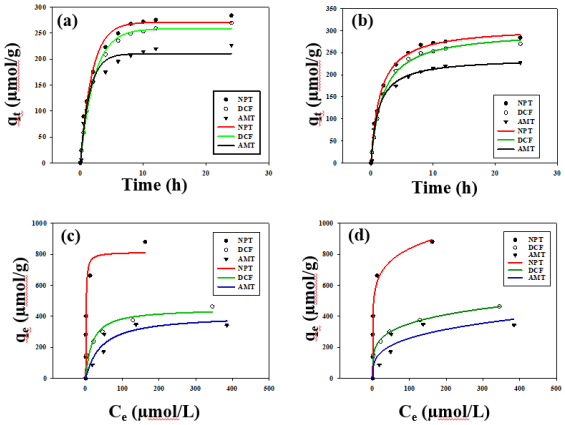

Figure 2. (a) Pseudo-first-order kinetics, (b) pseudo-second-order kinetics, (c) Langmuir isotherm model and (d) Freundlich isotherm model

Table 1. Kinetic and isotherm results.

model	pharmaceuticals	Parameters		
Pseudo-first-order kinetic		q_{e1} (µmol g^{-1})	k_1 (L min^{-1})	R^2
	1-Naphthol	271.13 (5.72)	0.54 (0.05)	0.989
	Diclofenac	258.69 (3.27)	0.45 (0.02)	0.999
	Amitriptyline	210.61 (6.01)	0.69 (0.09)	0.977
Pseudo-second-order kinetic		q_{e2} (µmol g^{-1})	K_2	R^2
	1-Naphthol	308.59 (4.48)	0.002 (0.0002)	0.997
	Diclofenac	299.98 (4.04)	0.002 (0.0001)	0.998
	Amitriptyline	237.89 (6.07)	0.004 (0.0005)	0.990
Langmuir isotherm		q_m (µmol g^{-1})	b (L µmol $^{-1}$)	R^2
	1-Naphthol	813.96 (134.99)	0.990 (0.91)	0.795
	Diclofenac	449.55 (61.45)	0.058 (0.04)	0.887
	Amitriptyline	409.59 (61.17)	0.024 (0.01)	0.911
Freundlich isotherm		K_F	n	R^2
	1-Naphthol	439.23 (129.81)	7.16 (3.69)	0.814
	Diclofenac	128.65 (5.84)	4.57 (0.19)	0.998
	Amitriptyline	68.19 (38.43)	3.46 (1.33)	0.831

Note: Braces figures represent standard errors.

The adsorption isotherm experiment were conducted to determine maximum adsorption capacity and sorption affinity of the composite fiber by taking different initial concentration (i.e. 50-500 µmol/L) of NPT, DCF, and AMT. The experimental data were modeled with Langmuir and Freundlich isotherm fitting (Zhao et al., 2021).The equations are shown below:

Langmuir model: $q_e = \frac{q_m b C_e}{1+bC_e}$ (5)

Freundlich model: $q_e = K_F C_e^n$ (6)

Where, q_m is the maximum adsorption capacity (µmol/g), q_e is the equilibrium adsorption capacity (µmol/g), C_e is the equilibrium concentration (µmol/L), b is the binding energy (L µmol^{-1}), K_F and n are the Freundlich constant. Fig.2c and d, reveal isotherms and table 1 shows isotherm parameters. The model fittings result that the experimental data are well fitted by Freundlich model in case of NPT and DCF with higher correlation coefficient (R^2) value while Langmuir model is best fitted in case of AMT with higher value of R^2. It indicates different adsorption mechanisms of AMT compared to NPT and DCF toward composite fiber.

Conclusion

Scavenger ACPEIA composite fiber was developed through a green approach for removal of ionic and neutral pharmaceuticals from neutral solution. The fiber demonstrated scavenging capacity for the removal of model cationic AMT, anionic DCF, and neutral NPT. Studied adsorption mechanism showed participation of hydrogen bonding, electrostatic interaction, and π-π interaction due to aromatic, amines, hydroxyl, and carboxyl parts. The scavenging ability of the fiber was due to the presence of all types of binding sites in the spongy composite holding cationic PEI, anionic alginate and aromatic AC linked through glutaraldehyde. Bearing scavenging power, the composite fiber could be a potential candidate to remove all types of water pollutants at neutral pH.

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