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Polymer/activated charcoal coated magnetite for the adsorptive removal of emerging contaminants: Stepwise synthesis via two sequential routes†

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Abstract: Emerging contaminants pose great health risks to humans and living organisms, even when released at minute concentrations over prolonged exposure times. In this work, we fabricate nanocomposites based on activated charcoal coated magnetite by incorporating the biopolymers of xylan or pectin into their structure. Two synthesis routes which differ in their sequential steps were investigated. It was demonstrated that the synthesis route affects the morphology, textural properties, and chemical structure of the nanocomposites, as confirmed by SEM imaging, BET analysis, and FTIR measurements, respectively. Hence, in turn, it influenced the performance of the nanocomposites in their adsorptive removal for the emerging contaminants of Fluoxetine and Famotidine whose presence in wastewater have been confirmed in several studies.

Keywords: emerging contaminant; synthesis; activated charcoal; polymer; magnetite

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1. Introduction

Emerging contaminants are a class of organic pollutants that can be hazardous to humans and living organisms when released in water bodies at minute concentrations over prolonged exposure times. One of the main concerns of their toxicities is that there is no regulatory framework that controls their levels in the environment. Emerging contaminants are classified into several categories including pharmaceuticals and personal care products, detergents, flame retardants, pesticides, etc [1]. This study is concerned with two pharmaceutical emerging contaminants, Fluoxetine HCl and Famotidine, which are found in surface water and in wastewater effluents of hospitals and pharmaceutical industries [2, 3]. Fluoxetine (FLX) is a selective serotonin reuptake inhibitor anti-depressant. It is present in surface waters at average concentrations of 0.012 μg/L, and in effluents of wastewater treatment plants at as high as 0.540 μg/L. FLX could induce developmental abnormalities in medaka fish by about 4-5 times higher than unexposed fish [4]. Famotidine (FAM) is a histamine blocker for the treatment of ulcers. It was detected in the effluent wastewater at concentrations of 410-5200 ng/L. Its risk quotient in algae and fish is 0.24 and <0.01, respectively [5].

Of the methods of great importance in the eradication of emerging contaminants from wastewater is adsorption owing to its effectiveness and operation flexibility [6]. Activated charcoal is one of the most popular adsorbents for wastewater treatment due to its high porosity and surface area which enhance the adsorption performance. However, it is difficult to handle during the treatment process and to remove from wastewater after treatment. Besides, it has a relatively high cost and can generate secondary pollutants [7]. Thus, we propose an environmentally-friendly approach to synthesize nanocomposite adsorbents by coating the activated charcoal over magnetite to enhance its separation by a magnetic field, then incorporating naturally abundant biopolymers, xylan and pectin, into this structure to enhance its biodegradability. The synthesis takes place by two routes that differ in the order of their sequential steps, to investigate the effect of the synthesis method on the characteristics of the prepared nanocomposites and their adsorption efficiency toward FLX and FAM. There exist very few reports in literature on the removal of these two contaminants, despite their alarming potential impacts on the environment [8, 9].

2. Materials and methods

1.1. Materials

Fluoxetine hydrochloride (FLX) of purity 100.3% (pKa 9.8) and Famotidine (FAM) of purity 99.9% (pKa 7.95) were cordially provided by Amoun Pharmaceutical Co., Cairo, Egypt. Activated charcoal (AC) was purchased from Adwic (part of Al-Nasr pharmaceutical chemicals company), Cairo, Egypt. Magnetic precursors of anhydrous ferric chloride (97%) and ferrous sulfate heptahydrate (98%), in addition to sodium hydroxide pellets (97%) were purchased from Fisher Scientific (part of Thermo Fisher Scientific), Germany. Purified beechwood xylan (4-O-methyl glucuronoxylan of purity>95%) with 12.8% glucuronic acid was purchased from Neogen Megazyme Ltd, Ireland. Pure pectin (poly-D-galacturonic acid methyl ester with M.W. of 25000 to 50000 Da) with >80% galacturonic acid and >7% methoxyl content was purchased from Sisco Research Laboratories Pvt. Ltd. (SRL), Maharashtra, India. Hydrochloric acid (37% by vol.) was purchased from Acros Organics-Fisher Scientific, Germany.

1.1. Preparation of the nanocomposites via synthesis route I

To prepare AC coated magnetite using synthesis route I (CM_{I}), a mass of 0.5 g AC was dispersed in 30 mL distilled water and stirred then 1.5 g ferrous sulfate heptahydrate and 1.75 g anhydrous ferric chloride were added and stirred for 20 min A 30% NaOH solution was added dropwise till the solution was black and stirred for 30 min. In case of xylan incorporated CM (XCM_{I}), a mass of 0.5 g xylan was dispersed in 95% ethanol and dissolved in 30 mL distilled water while heating and stirring till boiling. Once boiled, the heater was turned off and the solution was stirred for further 10 min then left to cool. A mass of 0.5 g AC was added and stirred for 50 min then the magnetic precursors were added as discussed above. Similarly, pectin incorporated CM (PCM_{I}) was prepared by dissolving a mass of 0.5 g pectin in 30 mL distilled water for 30 min then adding 0.5 g AC while stirring for 15 min before introducing the magnetic precursors. All the prepared nanocomposites were washed with distilled water three times and left in air to dry.

1.1. Preparation of nanocomposites via synthesis route II

To prepare AC coated magnetite using synthesis route II (CM_{II}), masses of 1.5 g ferrous sulfate heptahydrate and 1.75 g ferric chloride anhydrous were dispersed in 30 mL distilled water for 20 min then 30%NaOH was added dropwise till the solution was black and stirred for 30 min. A mass of 0.5 g AC was then added and stirred for 15 min. For XCM_{II}, a tank containing 0.5 g xylan in 15 mL distilled water was prepared as above and added to another tank of 30 mL CM_{II} then stirred for 50 min. Similarly, PCM_{II} was prepared separately where 0.5 g pectin was dissolved in 15 mL distilled water in a separate tank and added to the tank of 30 mL CM_{II} and stirred for 30 min. All the prepared nanocomposites were washed three times and left in air to dry.

1.1. Characterization of the prepared nanocomposites

FTIR measurements (Thermo Scientific Nicolet 380 FT-IR Spectrometer) for all nanocomposites were performed to determine the existing functional groups before and after adsorption. To examine surface morphology, SEM images (Zeiss Supra 55, UK) were taken after gold sputtering (Hummer™ 8.0, USA) at 15 mA for 1 min. To determine surface areas and pore volumes, BET measurements (ASAP 2020, Micrometrics equipment) were performed using nitrogen gas after degassing the samples at 40 °C for 8 h. For the determination of surface charge, DLS measurements were carried out using a Malvern Panalytical Zetasizer Nano-ZS90 (Malvern, UK).

1.1. Adsorption experiments

Batch adsorption experiments were performed for the removal of FLX and FAM using a rotary shaker at 60 rpm for 4 h. The applied initial concentration was 25 ppm and adsorption took place at pH 7.35 using 0.67 g/L of the nanocomposite at room temperature (25±2 °C). After adsorption, solutions were magnetically decanted and the supernatant was measured on UV/VIS spectrometer (Pg instruments, T80+ spectrometer, UK) at 228 and 275 nm for FLX and FAM, respectively. Obtained absorbances were substituted in the following equation: $\% \boldsymbol{Removal} = \frac{(\boldsymbol{A}_{\mathbf{i}} - \boldsymbol{A}_{\boldsymbol{f}})}{\boldsymbol{A}_{\mathbf{i}}} \boldsymbol{X100}$

where $\boldsymbol{A}_{\mathbf{i}}$ is the absorbance before adsorption and $\boldsymbol{A}_{\boldsymbol{f}}$ is the absorbance after adsorption [10].

1.1. Statistical analysis

All measurements were conducted in duplicate and expressed as mean ±SD error bars. Statistical analysis was performed using the paired two-tailed student's *t*-test at a 95% confidence level where p-values were calculated on Microsoft Excel 365 software.

3. Results and discussion

3.1. Characteristics of the prepared nanocomposites

Surface morphologies for the nanocomposites synthesized using the two routes are shown in Fig. 1. It is clear that the surfaces of XCMI and PCMI are rougher than CMI surface which appears to be relatively smooth and similar in morphology to activated carbons previously reported in literature [11]. The rough granular surfaces of XCMI and PCMI could be owed to the xylan or pectin polymer which probably coats the surface [12, 13]. On the other hand, XCMII and PCMII have almost the same morphology which is similar to that CMII, indicating that AC dominates the surface of these nanocomposites. These AC surfaces are similar to those reported in literature for commercial AC and AC derived from cluster stalks [14].

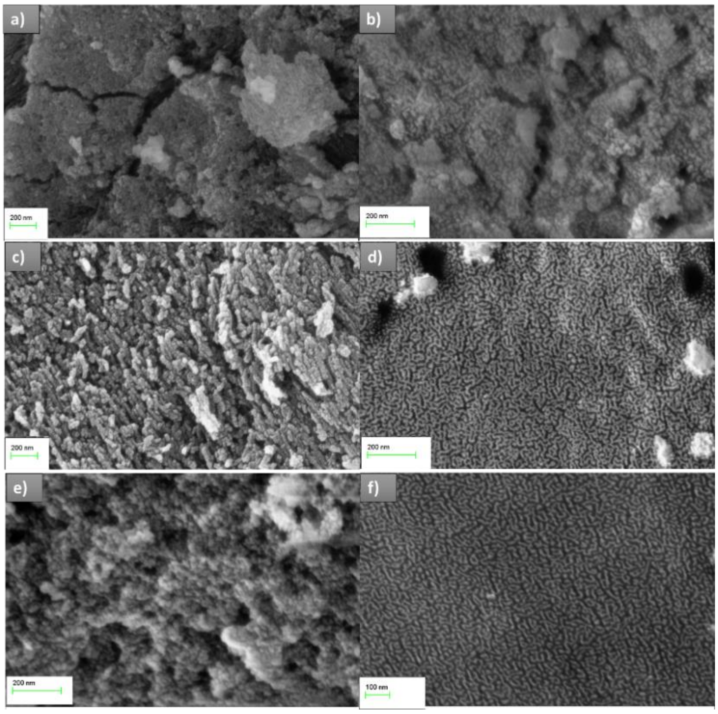

Figure 1. SEM images of (a) CMI, (b) CMII, (c) XCMI, (d) XCMII, (e) PCMI, and (f) PCMII.

The FTIR spectra of all nanocomposites (Fig. 2) show bands at about 3400 and 1630 cm^{-1} which could be assigned to OH and C=O groups of carboxylic acid [15]. For BET measurements, it is evident from Table 1 that the pore volumes of CMI and CMII are comparable while the surface area of CMI iss less than that of CMII by about 22% which indicate that magnetite blocked more surface pores on CMI. In the synthesis of CMI, the magnetic precursors are introduced as Fe ions to the AC, and hence have high diffusivity that can allow them to access more pores and complex with the pi electrons of the hydroxyl groups of AC [16]. In the synthsis of CMII, however, the magnetic precursors are introduced to AC as nanoparticles. This might also explain the lower FTIR peak intensity of OH shown for CMI (Fig. 2a) relative to its corresponding peak for CMII (Fig. 2b). This could have resulted from the involvement of the OH groups of CMI in more complexation bonding than their counterparts of CMII, and which in turn restricted their bond vibrations. Regarding the polymeric nanocomposites XCMI, PCMI, XCMII, and PCMII, they are not considerably different in their surface areas or pore volumes, but have lower areas and pore volumes than CMI and CMII. All the nanocomposites have pores that lie in the mesoporous range (2-50 nm), and they all have a negative surface charge at the working pH (Table 1).

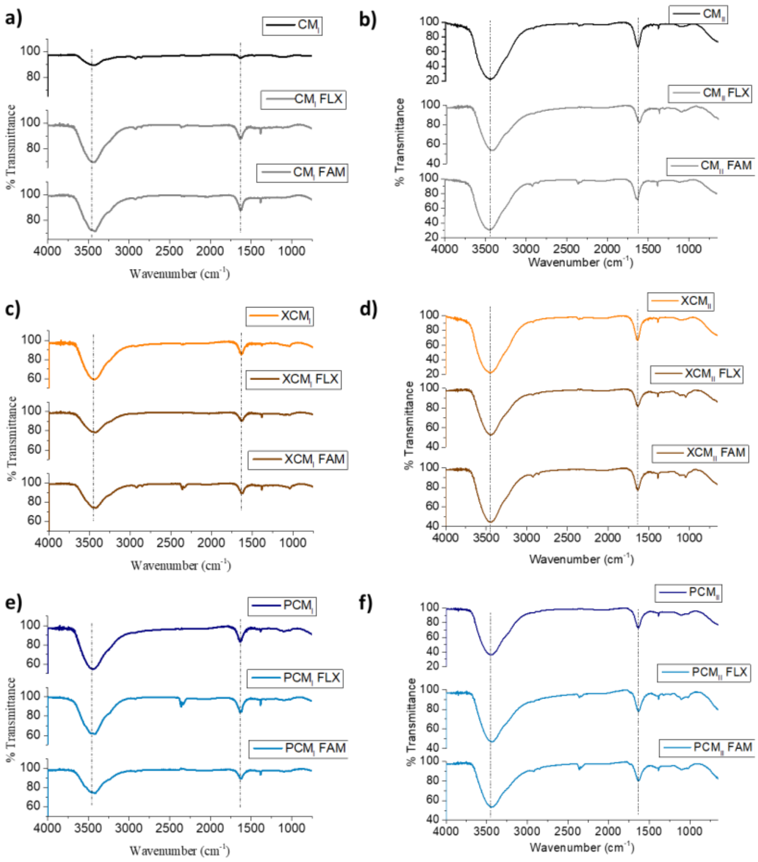

Figure 2. FTIR spectra of (a) CMI, (b) CMII, (c) XCMI, (d) XCMII, (e) PCMI, and (f) PCMII before and after adsorption of FLX and FAM.

Table 1. Textural properties and zeta potential of the nanocomposites.

	BET surface area (m^2/g)	BJH pore volume (cm^3/g)	Pore size (nm)	Zeta potential (mV)
CMI	348.7	0.25	5.71	-39.0
CMII	446.7	0.27	6.05	-29.8
CMI	227.1	0.16	6.07	-30.0
XCMII	219.8	0.13	6.33	-27.8
PCMI	227.5	0.16	5.56	-39.0
PCMII	266.3	0.19	7.14	-37.3

3.2. Adsorption performance

The adsorption performance of FLX and FAM on the prepared nanocomposites is depicted in Fig. 3. High removal percentages reaching 80-95% are obtained with pectin-based and AC-based composites. Generally, it is clearly shown that the composites synthesized by route II; CMII and PCMII, mostly exhibited a non-significant difference in %removal for FLX ($p > 0.05$), compared to the ones prepared using route I; CMI and PCMI, respectively, except for XCMI that gave an enhanced %removal by 27.6% ($p< 0.05$) than XCMII. However for FAM, only CMI and CMII showed a non-significant or comparable removal percent values ($p > 0.05$), while PCMII exhibited a lower percent removal than PCMI by 10.8% ($p< 0.05$), and XCMII showed a higher %removal than XCMI by 30.3% ($p< 0.05$). Though the removal percentages of FAM are apparently higher than those of FLX onto CMII, XCMII and PCMII, only XCMII showed a significantly higher percent removal for FAM than FLX ($p< 0.05$), unlike CMII and PCMII ($p > 0.05$). FLX binds more favorably to XCMI than XCMII, since xylan which coats the surface of XCMI provides polar functional groups that can capture FLX. However, FAM binds more favorably to XCMII than

XCMI since XCMII surfaces are dominated by hydrophobic centers that could adsorb the hydrophobic drug, which also explains the higher adsorption of FAM relative to FLX on the former nanocomposite. As for PCMI, the pectin dominating its surface provides both the polar functional groups and the hydrophobicity (being a methylated and galacturonated polymer) which can remove FAM with higher efficiency than PCMII.

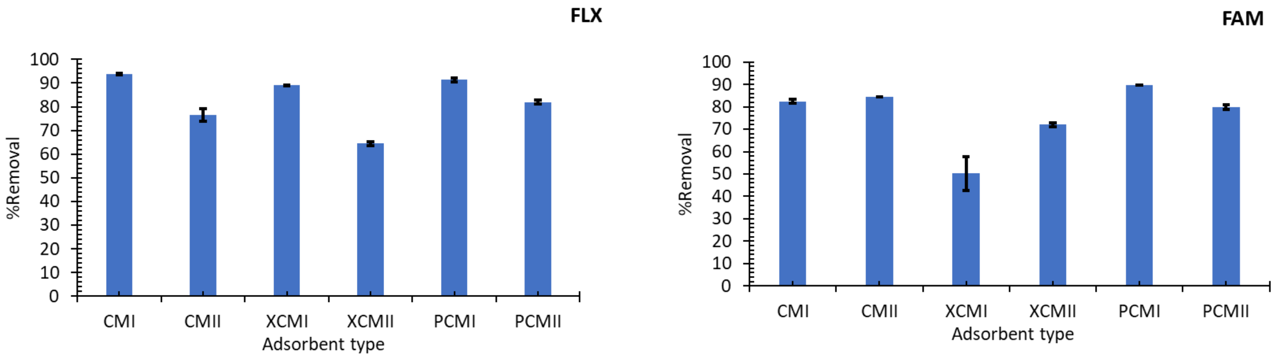

Figure 3. %Removal of (a) FLX and (b) FAM on the prepared nanocomposites at an initial concentration of 25 ppm, adsorbent dose of 0.67 g/L and pH 7.35. Values expressed as mean ± SD (*n* = 2).

3.3. Mechanism of adsorption

According to the zeta potential measurements at the working pH of 7.35 (Table 1), all nanocomposites are negatively charged and hence can interact with the positively-charged FLX (pKa 9.8) or FAM (pKa 7.95) via electrostatic interactions. The mechanism of adsorption of FLX and FAM on the nanocomposites has also been investigated through FTIR measurements before and after adsorption as depicted in Fig. 2. In composites prepared via route I, CMI showed an increase in the intensity of OH and C=O bands after FLX or FAM adsorption, however XCMI exhibited a decrease in the intensities of these bands. PCMI showed a shift and change in the intensity of OH band after FLX adsorption, while a shift in this band and the C=O band along with intensity change was encountered after FAM adsorption. For the composites synthesized by route II, CMII, XCMII and PCMII exhibited a clear change in the intensity of the OH and C=O bands after FLX or FAM adsorptions. These results manifest the role of hydroxyl and carboxylic acid groups in the adsorption of FLX and FAM from aqueous solutions possibly through electrostatic forces or hydrogen bonding. This does not negate the possibility of having hydrophobic interactions as well.

Conclusion

Successful preparation of biopolymer incorporated activated charcoal/magnetite nanocomposites was achieved via two different synthesis routes I and II. Nanocomposites prepared via synthesis route I had the biopolymer as the dominant coating on the surface, while those prepared via synthesis route II had the activated charcoal on the surface. Regarding removal efficiency, XCM nanocomposites prepared via synthesis route I exhibited better removal percentage of FLX and less removal for FAM when compared to their corresponding nanocomposites prepared via synthesis route II. Adsorption occurred mainly via electrostatic attractions beside other possible mechanisms of hydrophobic interactions and hydrogen bonding.

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