Application of Ag Nanoparticle Loaded Bio-based Activated Carbon Composites for Sequestration of Naproxen from Water

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In the present investigation we described a facile method to synthesize nano-silver supported activated carbon from renewable bio-resource and its eco-friendly promising role to purify pharmaceutical contaminated wastewaters. The adsorption characteristics of Naproxen (NAP) on Ag supported activated carbon (AAC) have been studied under varied environments. The developed adsorbent, AAC have been characterized by UV-Visible, FT-IR, SEM-EDXA, XRD, TEM and SAED. UV-Vis and TEM confirmed production of Ag NPs (average size of 15 ± 3 nm) on activated carbon surface. Further, XRD analysis authenticates the presence of pure face centered cubic (fcc) structure of silver nanoparticles formed on activated carbon surface. Various operational parameters, such as pH, adsorbent dose and contact time were optimized for the removal of NAP from water phase. The pseudo-second-order kinetic model was found to follow the adsorption phenomenon (with good correlation coefficient). The Langmuir isotherm well describes the experimental data and maximum monolayer adsorption capacity was 200 mg/g for AAC. The pH and optimal temperature for adsorption process are found to be 4.0 and 303 K, respectively. The rate of adsorption is remarkably fast at the beginning and achieves equilibrium in 120 min. The obtained results showed that AAC was a better substitute as composite materials for remediation of wastewater.

Introduction

There has been an enormous rise in the consumption of pharmaceutical drug over the last few decades and consequentially their occurrence in aquatic regions and drinking water supplies have also spiraled up without precedence. Large numbers of pharmaceuticals including naproxen were continuously introduced into aqueous systems and have large effect on drinking water.[1] It was evident from the literature that adsorption process was better substitute for remediation of naproxen from water phase.[2–5] The main objective is to study the potential feasibility of silver nanoparticles supported activated carbon developed from renewable bio-resource for remediation of naproxen from water phase.

Materials and Methods

Naproxen (purity: 99%) was obtained from Sigma-Aldrich Chemicals Private Limited and selected as a model contaminant. A total of 40 ml of Agar wood (*Aquilaria agallocha*) leaf extract was added to a 10 ml of freshly prepared $AgNO_3$ (0.1 M aqueous solution) at 343 K for 10 minute and then slowly cooled at room temperature. After 3 days of time, brown sediments were formed and confirmed the formation of silver nano-particles (Ag NPs). Then the brown solution was centrifuged and filtered and residues obtained were washed with double distilled water to eliminate any impurities. The precursor, *Schumannianthus dichotomus* (SD) for preparation of activated carbon was reported elsewhere.[6]

A total of 80 mL of freshly prepared Ag NPs was mixed with developed activated carbon (10g) in a 250 mL flask and magnetically stirred upto 6 h. These result into the deposition of Ag NPs on activated carbon. The Ag loaded activated carbon was filtered and washed several times with double distilled water. The obtained Ag NPs-ASD powders were grounded homogeneously with motor-pastel and designated as silver loaded activated carbon (AAC). The remaining concentration of naproxen was monitored at a maximum absorbance of 230 nm by UV-Vis Spectrophotometer (Thermo Scientific).

Results and Discussion

The Ag NPs shows a distinctive UV-Visible adsorption band known as localized surface plasmon resonance. The UV-Visible spectra of as-synthesized Ag NPs showed the formation of Ag NPs. The optical

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characteristics of Ag NPs confirm variation of their morphology (shape and size). The surface plasmon vibrations of spherical Ag NPs mainly indicate the presence of absorption band at ~420 nm.

FT-IR investigation showed the presence of peak at 3437 cm^{-1} and assigned for hydroxyl (-OH) group. The peak position at 1718 cm^{-1} is assigned for C=O group of carboxylic acids. The presence of C–O stretching in carboxyl was evident from the absorption peak obtained at 1361 cm^{-1}. The lower absorption bands at 498 and 454 cm^{-1} may be allocated to Ag-C/N bond.

The elemental analysis of silver supported activated carbons was analyzed by EDX and indicated the existence of Ag, C and O on the surface of the adsorbent. The XRD patterns of Ag NPs showed a face-centered-cubic (fcc) structure as evident from diffraction peaks at 38.19^0, 44.32^0 4.75^0 and 77.12^0 corresponds with diffraction from (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes, respectively. Scherrer formula was used to calculate the average crystallite size and found to be 14.05 nm. The appearance of peaks for activated carbon and the sharp peaks of silver indicated the co-existence of both silver nanoparticles and activated carbon on AAC. The full width at half-maximum (FWHM) of the (1 1 1) peaks of Ag NPs are found to be the same (before and after being loaded onto AC) indicates that size of nano particles remain same. The morphology of the nano-sized silver particles showed a spherical shape as observed from TEM investigation. Further, TEM observations indicated that the mean size of particles was about 15 ± 3 nm. The rings in electron diffraction pattern may be assigned to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes and well matched with JCPDS file No. (87-0720) and corresponds to crystal planes of an fcc

lattice structure. The TEM micrograph of AAC is displayed in Fig. 1 (a-c). The morphology of AAC was different from that of AC as evident from the TEM micrograph. The developed Ag NPs loaded activated carbon composites (AAC) was found to have flower-shaped morphology.

The equilibrium adsorption of NAP by AAC is described by Freundlich, Langmuir, Temkin and DR adsorption models at all studied temperatures, such as 303, 313 and 323 K. The Langmuir model satisfactorily explained adsorption experimental data at all studied temperatures (linear regression coefficient values ranges from 0.9180 to 0.9870). Whereas, the Temkin and DR model shows poor fitting to the experimental data as the LRC values are in the range of (0.7240~0.8800) and (0.4110 ~0.6370) for Temkin and DR, respectively. The validity of different isotherms model and the various error functions are also computed to find out the best model and shown in Table 1.

The impact of acidity for naproxen removal was investigated with AAC. To assess the effect of the influence of pH on the removal of naproxen, experiments were run with an initial concentration of 20 mg.L^{-1}, temperature of 303 ± 3K, agitation speed of 160 ± 10 rpm, and interaction time of 120 min at varying solution pH. As the pH changes from acidic to basic region, % removal reduces from 95.56% (at pH 4) to almost 75% (at pH 8). Naproxen is an acidic pharmaceutical compound with a pK$_a$ value of 4.2 and predominantly exists as neutral molecules at a pH of 4.2 and as NAP-H$^-$ at a pH greater than 4.2. The uptake of NAP on the surface of AAC is mainly due to the electrostatic, and/ or non electrostatic interaction and depends on solution acidity. The adsorption is not favoured with increase in
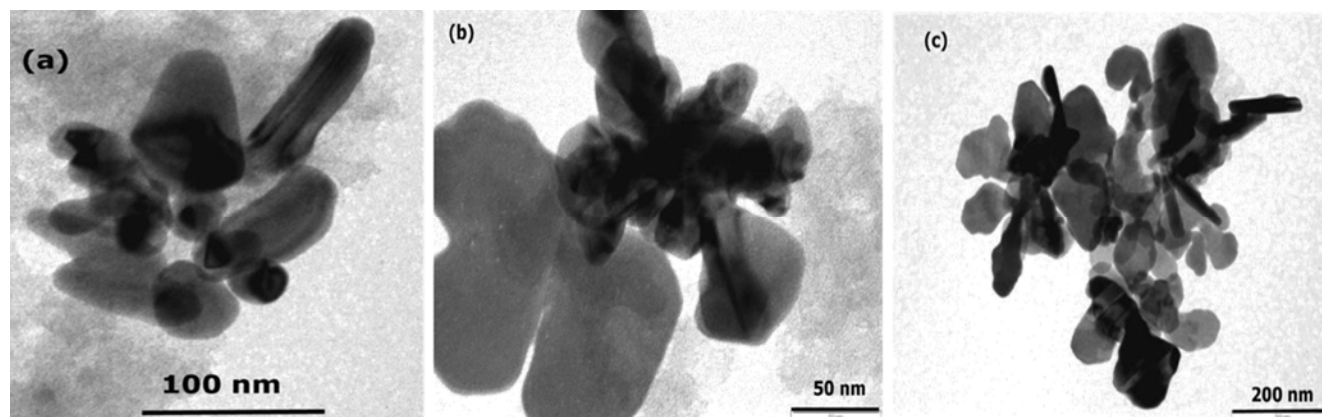

Fig. 1 — (a–c) TEM images of AAC

Table 1 — Isotherm parameters for adsorption of NAP onto AAC

Isotherm	Temperature(K)	Parameters			R^2
		$a_L(mg.g^{-1})$	$b_L(L.g^{-1})$	RL	
	303	200.00	0.1086	0.31	0.9440
Langmuir	313	23.80	0.3890	0.11	0.9780
	323	29.11	0.0854	0.36	0.9000
		$1/n_F$	$k_F(mg.g^{-1})$	—	
	303	0.80	10.00	—	0.9180
Freundlich	313	0.30	42.65	—	0.9870
	323	0.14	2.57	—	0.9540
		$B(J.mol^{-1})$	$K_{Tem}(L.g^{-1})$	—	
	303	48.77	1.26	—	0.8800
Temkin	313	29.22	2.07	—	0.7520
	323	39.26	4.68	—	0.7240
		Ψ_D	ϕ_D	—	
DR	303	1.90	70.80	—	0.4110
	313	43.34	126.46	—	0.5630
	323	223.10	77.80	—	0.6370

solution pH ($<pK_a$) because of electrostatic repulsion of NAP with adsorbent surface. On the contrary, at a lower pH (> 4.2) strong interaction of NAP with active site of AAC favoured adsorption. Therefore, it can be concluded that the removal of NAP is favourable in acidic region.

To optimize the load of adsorbent, experiments were conducted with 20 mL of NAP solution (20 mg.L^{-1}) at varying adsorbent dose. The adsorption of NAP was exceptionally increased upto 1.2 g.L^{-1} and afterwards, a plateau has reached. The adsorption efficacy remains unaltered with additional increase in load of the adsorbent. Initially, large concentration of NAP in their bulk solution enhanced adsorption affinity towards unoccupied site of ACC and demonstrated that equilibrium of NAP molecules on AAC surface is achieved.

Experiments were also conducted to assess the impact of interaction time for removal of NAP. A total of 82.65 % removal of NAP was observed within initial interaction time of 20 minute followed by marginal increase of adsorption with time upto 120 minute. The quasi-equilibrium was attained within 60 minute of interaction. Thus, optimal time to perform the subsequent adsorption experiments was chosen at 60 minute. The values of kinetic constants for adsorption of NAP onto AAC are presented in Table 2. Good regression coefficients and validity of different kinetic models showed that removal process obeyed the pseudo-second order for adsorption of NAP. The negative value of standard enthalpy ($\Delta H° = -36.24$ kJ.mol^{-1} for AAC) showed the adsorption

Table 2 — Kinetic models parameters for adsorption of NAP onto AAC

Kinetic model	Model parameters	Values
Pseudo- first order	$q_{e, exp}$ (mg.g^{-1})	10.26
	$q_{e, cal}$(mg.g^{-1})	4.45
	k_1(g.mg^{-1}. min^{-1})	0.006
	R^2	0.8977
	$\Delta q\%$	17.07
Pseudo-second order	$q_{e, cal}$(mg.g^{-1})	9.90
	k_2 (g.mg.min^{-1})	0.01
	R^2	0.9990
	$\Delta q\%$	1.05
Liquid film diffusion	k_{fd} (min^{-1})	−5.6
	Ifd	−0.9039
	R^2	0.934

process was exothermic in nature. The standard entropy ($\Delta S°$) value was also observed to be negative and signifies the decrease in randomness of the adsorption with no changes occurring at the liquid/solid interface. The negative value of Gibbs free energy confirmed that adsorption of NAP on studied adsorbent was spontaneous and thermodynamically favourable.

Conclusions

A new composite material (AAC) has been developed from renewable bio-resource and utilized for the removal of NAP from aqueous phase. The equilibrium adsorption data for adsorption of NAP on AAC is found to be in good agreement with the Langmuir isotherm model. The kinetic of adsorption

process may be effectively fitted to the second-order kinetic model with involvement of intra-particle diffusion model. The theoretical monolayer adsorption capacity for removal of NAP was obtained at 200 mg/g. The removal percentage of more than 82% was achieved within 20 min of interaction time for NAP adsorption onto AAC.

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