Enhanced removal of ciprofloxacin using humic acid modified hydrogel beads

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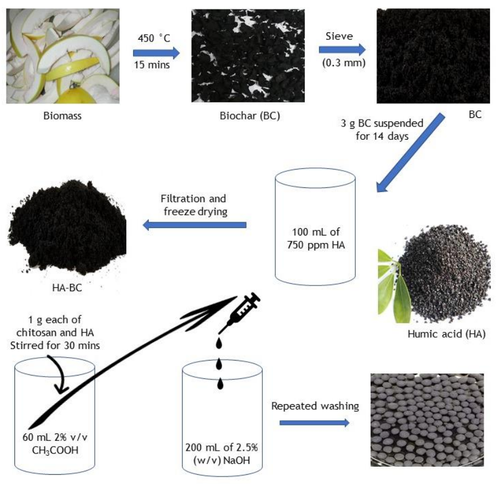
Widely present Fluoroquinolones (FQs) in wastewater, due to their high production and incomplete metabolization, provoke antibiotic resistant bacteria resulting in various health disorders.

We prepared an adsorbent for ciprofloxacin by incorporating humic acid on powder biochar (to add more functional groups) followed by encapsulation in chitosan to covert it into beads which are stronger, separable, and recyclable.

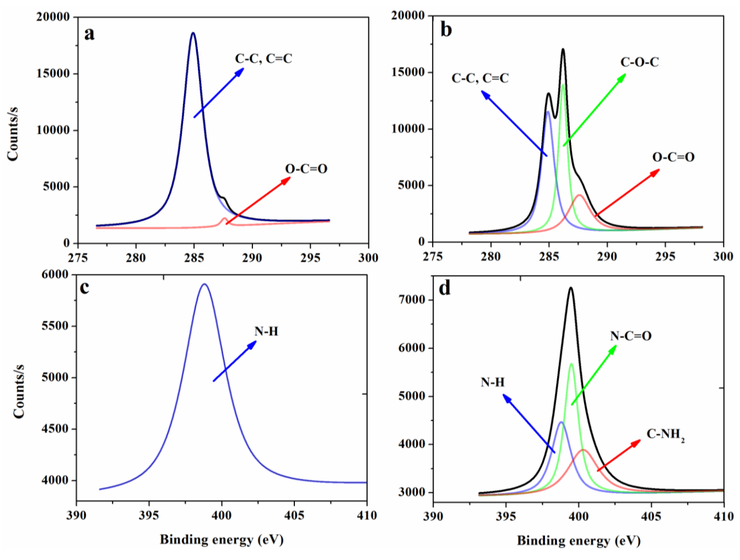
Biochar (BC) has wide range of applications in environmental remediation, and many studies have confirmed that its surface modifications can enhance its sorption capacity.



Flow chart of adsorbent (HBCB) preparation.

Humic acid (HA) has a complicated macromolecular structure, with many hydrophilic groups (including carboxyl, hydroxyl, phenolic, alcoholic, amide and amine) covalently bonded to hydrophobic groups (including aliphatic, aromatic and heterocyclic structures.

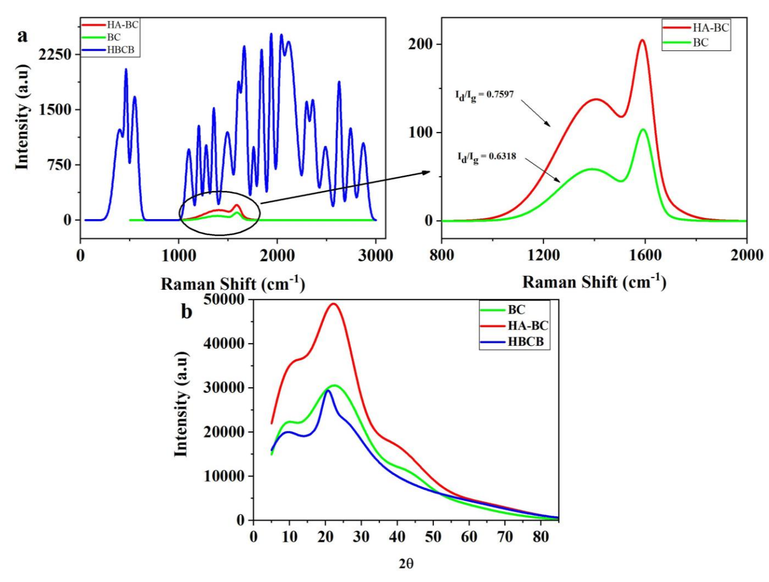
Therefore, modification of BC with HA looks very promising approach. At the same time, due to difficulty in separation of the composite from suspension, there is an urgent need to assemble an effective three-dimensional structure with the composite material, for sustainable use.



C 1s and N 1s core spectra of HBCB pre and post adsorption

Presence of two Raman peaks at 1360–1380 cm^{-1} and 1570–1590 cm^{-1}, correspond to the D-band and G-band of sp^2 type carbon. Increase in Id/Ig ratio from 0.6318 (BC) to 0.7597 (HA-BC) reflects a decrease in the average size of sp^2 domains and increase in number of functional groups and creation of new graphitic domains of a smaller size and higher frequency.

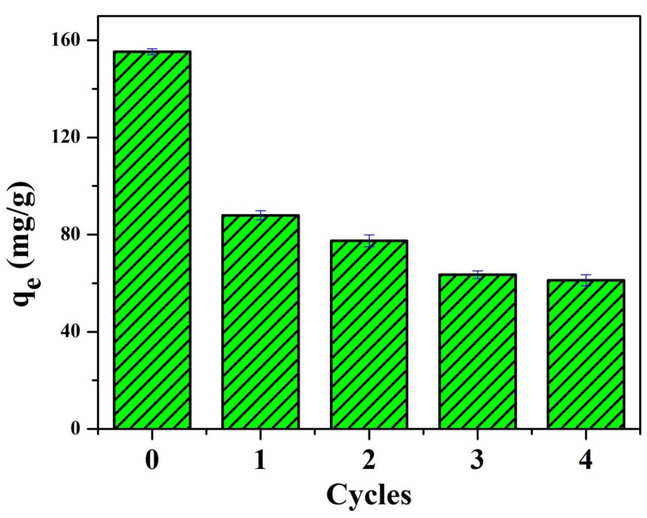
Broad XRD peaks at 23° and at 43° are considered characteristic peaks of graphitic carbon, and at 9° indicates presence of oxygen containing functional groups and interspersed water molecules. Increase in intensities of peaks after incorporation of HA indicates enhancement of functional groups already present on BC.



(a) Raman spectra and
(b) XRD spectra of BC, HA-BC, and HBCB (before adsorption).

Both C1s and N1s core spectra of adsorbent (post adsorption) of CIP indicates generation of new peak at 286.2 eV (C–O–C), 399.5 eV (N–C=O) and at 400.3 eV (C–NH_2).

Adsorption capacity of 154.89 mg/g in first cycle was still enough (60 mg/g) after 4th regeneration cycle. Therefore, HBCB can be an economical adsorbent for the removal of CIP from wastewater.



Adsorption capacities of HBCB in different regeneration cycles.

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