Bio-Based Phosphate Functionalized Activated Carbon from Indian Gooseberry Seed Shells for the Efficient Copper (II) Adsorption

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Abstract
Preparation of an efficient activated carbon for the removal of metal pollutants is a challenging research today. The characteristic features of an efficient phosphate functionalized activated carbon, synthesized by following chemical activation process followed by subsequent functionalization from Indian gooseberry seed shells for the copper (II) adsorption are reported. Indian gooseberry seed shells based activated carbon showed the BET surface area of 1359 m²/g, the adsorption capacity of 44.84 mg/g at 30 °C and at a pH value of 9.52. The adsorption process was satisfied by the pseudo-second-order kinetic model along with the Langmuir adsorption isotherm. This AC could be used as a favorable and cost-effective copper (II) adsorbent in wastewater treatment to remove the metal contaminants.

Keywords: Activated carbon, Adsorption isotherm, Kinetic model, Characterization.

1. Introduction
Adsorption is one of the most efficient process to remove copper from the contaminated water. Synthesis of the new cost-effective and efficient adsorbent for the removal of the harmful contaminants is a challenge to the researchers. Activated carbons (ACs) are extensively used by the industries as an efficient and effective adsorbent for its high surface area and high pore volumes. The physical and chemical properties of the ACs are depended mainly on the characteristics of the precursor materials. The researchers are trying to find out the appropriate precursor materials for the synthesis of the ACs. The ACs prepared from sewage sludge (Wang), hazelnut shell (Demirbas), cassava peel (Pirajan), Tunisian date stones (Bouhamed), grape bagasse (Demiral), pecan shell (Shawabkeh), chestnut shell and grape seeds (Ozcimen), hazelnut husks (Imamoglu), peanut shells (Wilson), ceiba pentandra (Rao) and apricot stone (Koby) were utilized as the copper adsorbent. The present work aims to synthesize an effective and cost-efficient copper adsorbent. The parametric effects of the initial pH and contact time at room temperature on the adsorption capacity were investigated. The adsorption isotherms and kinetics of the copper adsorption onto the activated carbon (AC) from the Indian gooseberry seedshells (GB10) were analyzed based on the experimental results.

2. Materials and Methods
AC was prepared from the Indian gooseberry seed shells by chemical activation and subsequent functionalization. The gooseberries were collected from the local market and peel it off to get the seed shells, washed with the water thoroughly, and then cuts into pieces and finally dried in a hot air oven at 95 °C for 5 days and used as the precursor material. The dried sample is then impregnated with the activating agent (50% diluted H₃PO₄ (85%)) solution at a ratio of 1:4 at room temperature (30 °C) for 16-18 hours. The sample was carbonized at 500 °C for 1 hour at a heating rate of 10 °C/min. in a silica crucible and designated as GB10W. The carbonized sample was activated again or functionalized in the pure H₃PO₄ (85%) at 95 °C and was designated as GB10. The prepared AC was then washed and dried.

The copper solution (100 mg/l) was prepared by dissolving copper sulfate pentahydrate (CuSO₄, 5H₂O) salt in milli-Q water. The various pHs (pHs values were 3.06, 5.20 and 9.52) of the solutions were maintained by adding 0.1 M HCl and 0.1 M NaOH solution to the initial solutions. Then the batch adsorption studies were performed by taking 0.02 g of AC samples in each case.

3. Results and Discussion
3.1. Characterization
The surface area and porosity of the derived ACs from the gooseberry seed shells after carbonization and after the secondary activation or functionalization was examined by the N₂ adsorption-desorption isotherms (Fig. 1). The AC prepared from the gooseberry seed shells (GB10) exhibited a type-I isotherm and H4 type of hysteresis loop with the BET surface area of 1359 m²/g.
The AC samples show three significant peaks at 1305 – 1360 cm$^{-1}$ (D-band), 1540 – 1575 cm$^{-1}$ (G-band) and 2750 – 2845 cm$^{-1}$ (2D-band). $I_D/I_G$ ratios greater than one ($I_D/I_G = 1.38 – 4.50$) indicate the multilayer formation. The sample GB10 was amorphous, multilayered and sp$^2$-hybridized graphitic carbon ($I_D/I_G = 0.98$ and $I_D/I_{2D} = 3.32$) as illustrated in Fig. 4. The FE-SEM photograph of GB10W (Fig. 5(a)), showed the presence of irregular porous surface affected by the $H_2PO_4$ during the carbonization. During the functionalization with pure 85% $H_2PO_4$, the acid attacks the pore increasing the mesopore volume and forming the well developed pores (Fig. 5(b)). Fig. 5(c), shows the FE-SEM photograph of GB10 after the adsorption.

3.2. Adsorption Studies

3.2.1. Effect of initial pH on adsorption

The copper adsorption capacity increased from 18.70 mg/g to 44.84 mg/g with the increase of pH from 3.06 to 9.52 (Fig. 6). The adsorption rate decreased with the increasing time. In acidic solution, the smaller $H^+$ ions having the higher mobility towards the adsorption sites reduce the $Cu^{2+}$ adsorption. Some functional groups ($OH^-$ or $PO_4^{3-}$) can also make the surface of the AC negatively charged, can increase the copper adsorption. The highest
copper (II) adsorption capacity obtained by the AC (GB10) at a pH value of 9.52 at 30 °C temperature.

![Fig. 7. Pseudo-second-order kinetic model.](image1)

The adsorption capacities of the ACs were determined with the differences in copper concentrations in the initial and final solutions.

![Fig. 8. Langmuir adsorption isotherm.](image2)

4. Conclusion

The AC prepared from the Indian gooseberry seed shells showed the maximum copper adsorption capacity of 44.84 mg/g at 30 °C and a pH value of 9.52. The experimental data were satisfied by the pseudo-second-order kinetics and the Langmuir isotherm model. The results stated that the AC synthesized from the gooseberry seed shells and functionalized with phosphate groups may be used significantly as a cost-effective and efficient copper (II) adsorbent.

3.2.2. Adsorption kinetics and isotherms

The copper adsorption onto the synthesized AC followed the pseudo-second-order kinetics ($R^2 = 0.997$) and Langmuir adsorption isotherm model ($R^2 = 0.990$) satisfactorily. The models are represented as follows

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e}$$

(1)

$$\frac{C}{q_e} = \frac{1}{bQ_m} + \frac{C}{Q_m}$$

(2)

In Eq. (1), $k_2 (0.0008 \text{ g/mg min})$ is the pseudo-second-order rate constant and $t$ is the time (min). $q_e$ (48.52 mg/g) and $q_t$ are the amount of copper (II) adsorbed at equilibrium and time $t$ respectively (Fig. 7). $b (0.195 \text{ l/mg})$ is the adsorption equilibrium constant, $Q_m$ is the maximum adsorptivity (47.60 mg/g) and $C_e$ is the solution concentration at equilibrium (mg/l), shown in Fig. 8. The maximum adsorption capacity of 47.60 mg/g, closely resembles our experimental data 44.84 mg/g.

References


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