PREPARATION, SURFACE FUNCTIONALIZATION AND CHARACTERIZATION OF CARBON MICRO AND NANO FIBERS IN ADSORPTION APPLICATIONS

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Introduction

Adsorption has shown considerable potential in environmental remediation applications, especially if the concentration levels of contaminants are in low levels, i.e., parts per million (ppm) or sub-ppm level. The viability of such technique is greatly dependent on the development of suitable adsorptive materials. In this study, we describe the synthesis of hierarchal web of carbon micro and nanofibers functionalized to incorporate acidic or basic surface functional groups by chemical methods. The prepared materials were applied as adsorbents for the control of Pb, phenol, and dye in wastewater and that of 2-dichloroethanol, a persistent organic compound in the gaseous phase.

Experimental

The raw samples of the phenolic resin precursor based non-activated carbon fibers (ACFs) were imported from Kynol, Japan. Steam was used as an activation agent. The as-received samples were first dried under vacuum and at a temperature of 300 ^{o}C to drive off moisture and other impurities from the fibers. Carbonization was carried out at around 950 ^{o}C in an inert atmosphere, whereas activation temperature was set at 850 ^{o}C.

Acetone was used as a solvent for nickel nitrate salts (0.4 M) for the impregnation of ACF. Refer Figure 1. ACF were wrapped on a perforated tube which was co-axially and vertically fitted in a tubular shell. Impregnation was carried out under continuous flow of the solvent using a peristaltic pump for 6 h. After impregnation, the sample was air-dried for 6 hours, and then for another 6 hours at 150 ^{o}C inside an oven to remove moisture. It was subsequently calcined at 300 ^{o}C for 2 h. During calcination Ni(NO$_3$)$_2$ was converted into NiO. The resulting metal oxide was then reduced to the corresponding metallic state by treating it in a hydrogen flow at 0.16 slpm at 500 ^{o}C for one hour.

After reduction, nitrogen was bubbled through benzene and passed through the adsorber packed with metal impregnated ACF. A Freon refrigeration unit was used for controlling the temperature of the bubbler, thereby setting the saturation vapor pressure of the liquid benzene and therefore, the desired concentration of the benzene vapor in the carrier gas. Benzene saturated nitrogen was passed through the reactor maintained at 750 ^{o}C. This resulted in the decomposition of benzene at the active Ni catalyst sites to carbon and subsequent formation and growth of CNF. The chemical vapor deposition (CVD) of benzene was continued for one hour after which the system was allowed to cool down to room temperature by purging the system with nitrogen. The detailed configuration of the adsorber and the procedure are available in [1].

The ACF-CNF composites form a hierarchy of pores as well as fiber size. The prepared hierarchal web of ACF/CNF was subsequently sonicated in acidic medium of various concentrations and times to open the pore-mouth. The prepared material was also functionalized with different reagents to incorporate different functional groups in certain end-applications, for example, with aq. ammonia in removing phenol, HNO$_3$ in removing Pb, and with pyridine to remove 2-dichloroethanol. All adsorption tests were performed under batch as well as flow conditions.

The concentrations of phenol and methylene blue (MB) dye were measured by Varian make UV-Vis spectrophotometer. The measurement of Pb was carried out using METROHM Ion Chromatography (IC). 2-dichloroethanol was measured by Nucon make gas chromatography with thermal conductivity detector.

Results and Discussion

The specific surface area and pore volume of treated and untreated ACF samples were measured using a BET analyzer supplied by Smart Instrument Ltd. (model no: Smart Sorb 92/ 93). Surface area was calculated from the experimentally obtained N$_2$ adsorption isotherm over the relative pressure range of 0.01 to 0.3, using the standard Brunauer, Emmett, and Teller (BET) method. It was observed that on impregnation of ACF with Ni, the BET area as well as the pore volume decreased significantly. The significant decrease in BET area of ACF-Ni sample was observed as a result of the coverage of most of ACF micropores by catalyst deposition. A marginal increase in the BET area of CNF was observed due to the formation of CNF.

Fig. 2a is the SEM image of as-received ACF samples. Figs. 2b, 4c, and 4d are the SEM images of 0.4(M) Ni-impregnated ACF, and ACF/CNF at different magnifications. It may be observed that fine nano sized Ni particles were uniformly distributed on the surface of the fiber. The growth of CNF may be seen everywhere on ACF. The nickel particles may be observed at the tip of the nanofibers. After sonication, most of the particles were removed from the tips or distributed over the fibers surface.

The concentration of solute in the solid phase was theoretically determined by the mass balance: $q=V*(C0-C)/w$, where $C0$ and C are the aqueous phase solute concentrations before and after equilibrium was attained. V is the volume of the solution in contact with the adsorbents of weight w. Fig. 3

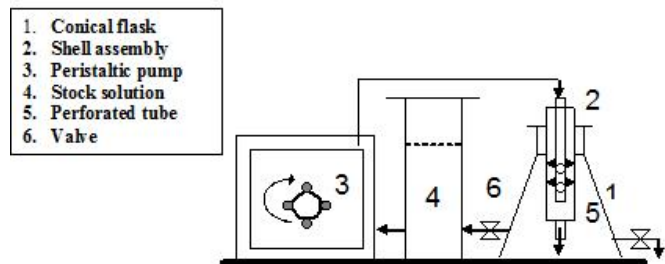represents the equilibrium isotherms for lead for vacuum dried

Fig1. : Experimental set up for impregnation of ACF with nickel nitrate.

1. Conical flask
2. Shell assembly
3. Peristaltic pump
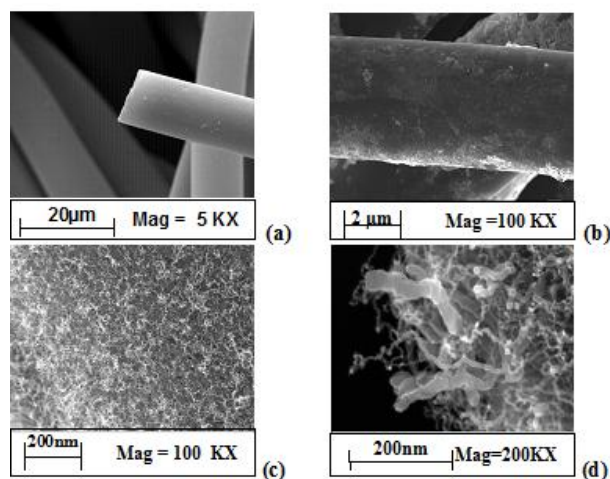4. Stock solution
5. Perforated tube
6. Valve

Figure 2: SEM image of (a) ACF, (b) impregnated ACF, (c) & (d) CNF

ACF, Ni-ACF/CNF and acid sonicated ACF/CNF. It was observed that ACF/CNF had larger adsorption capacity than that of the vacuum dried ACF and the acid (HNO$_3$) treated ACF/CNF had larger capacity than that of CNF. Sonication in acidic medium had dual effects. Acid sonication resulted in the removal of nickel present on the tips of nanofibers. Additionally, oxidation by HNO$_3$ caused an increase in the cation-exchange capacity of carbon [2]. The similar effects were observed for the removal of 2-dichloroethanol by the prepared hierarchal web of carbon micro/nanofibers. Pyridine functionalized ACF/CNF performed better than the other adsorsbents.

Interestingly, the ammonia treated ACF gave optimum results for phenol removal. The relatively larger size of phenol molecules could not sufficiently penetrate the pores of nanofibers. Nitrogen containing surface groups were responsible for the increased basicity of adsorbent making the adsorption of acidic phenol relatively more favorable [3]. Similarly, the equilibrium loading of MB was observed to be larger on ACF than on ACF/CNF sample. However, the equilibrium loading of MB is larger on the ACF functionalized with H$_2$O$_2$ compared to ACF and CNF. This is due to the

incorporation of oxygen functional groups such as carboxylic, carbonyls and quinone groups on the surface of ACF.
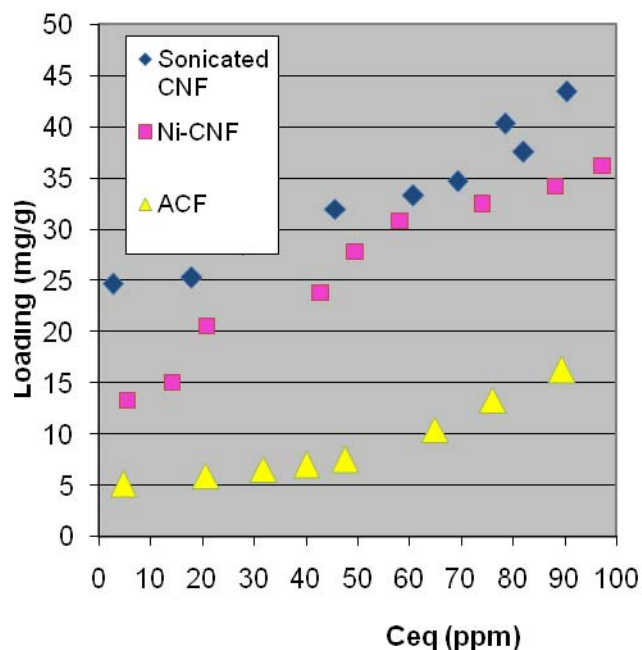

Fig.3 Comparative equilibrium loading of Pb on various adsorbents

Conclusions

This study demonstrates that CNF may be synthesized uniformly and densely on ACF fabrics, by catalytic chemical vapor deposition using nickel as a catalyst. Adsorption tests revealed the signficant adsorptive capacity of acidic/basic functionalized ACF/CNF in the removal of lead, phenol, MB, and 2-dichloroethanol. The effects of pore structure, pore size distribution and the presence of surface functional groups are important in adsorption.

References
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