INFLUENCE OF SURFACE TREATMENT ON NICKEL (II) ION ADSORPTION OF STACKED-CUP TYPE CARBON NANOFIBERS

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Influence of Surface Treatment on Nickel (II) Ion Adsorption of Stacked-cup Type Carbon Nanofibers

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Abstract. Influence of surface oxygen functional group (SOFG) of stacked-cup carbon nanofibers (CNFs) as adsorbents for nickel (II) ion was investigated. The SOFG was introduced onto the original CNFs surface by treating the fiber with concentrated nitric acid solution for 3 hours. Adsorption study was carried out using nickel aqueous solutions of from 100 to 900 mg/L concentrations and contact time range from 60 to 180 minutes. The presence of SOFG was studied by FTIR spectroscopy. Field emission scanning electron microscopy was then used to characterize the morphology of the CNFs. Langmuir and Freundlich adsorption isotherm models showed that the acid modification which increases the number of oxygen functional groups on the fiber surface improves the nickel ion adsorption capacity.

Introduction

Nickel is one of the elements which is widely used in many industrial applications such as shipbuilding, automobile, electrical, oil, food and chemical industries. As a result of these activities, nickel is a common pollutant in many industrial wastewaters. The main sources of nickel pollution include cruise ships, industrial application and chemical industry effluents. Nickel in untreated industrial wastewaters can be adsorbed and/or accumulated by living organisms directly or indirectly through their food chains. Its organic forms are much more toxic than the inorganic compounds. Nickel causes skin irritant, is toxic to the cardiovascular system, and carcinogenic [1]. Many techniques have been proposed for nickel and other heavy metals removal from wastewaters. These include chemical oxidation or reduction [2], chemical precipitation [3], ion exchange [4], membrane separation [5], filtration [6], electrochemical treatment [7] and adsorption [8,9]. Adsorption is widely applied due to its low cost and high efficiency compared to the other conventional methods. Removal of heavy metals by carbon materials such as activated carbon [10,11,12] and carbon nanotubes [13,14,15] has been studied

Results and Discussion

The objective of the oxidization process is to modify the surface of the CNFs, specifically to increase the amount of surface oxygen functional groups (SOFG) of the carbon nanofibers [18, 19]. The oxidation process increases the CNFs surface hydrophilicity which consequently enhances the CNFs dispersion in polar solvents. Moreover, the SOFG provide anchoring sites for adsorption of metals ions and large molecules [20]. Figure 1 shows that the presence of significant higher amount of oxygen species on the oxidized CNFS surface in comparison to that of the commercial CNFs. Intensive band at 3417 cm^{-1} represents hydroxyl groups of carboxylic acid or alcohol (21). The C=O bands characteristic of ketone/quinone are observed at 1630 cm^{-1}. New peaks appear at 1518, 1463 and 1380 cm^{-1} in oxidized CNFs corresponds to absorbed water (OH in-plane deformation) and the presence of C-O bonds in various chemical surroundings [21]. Peaks at 1082 cm^{-1} and 1013 cm^{-1} are assigned to the stretching vibration of C-O and -O-H bending in carboxylic acid and phenolic groups. These groups are expected to be the active sites for nickel ion adsorption [5].

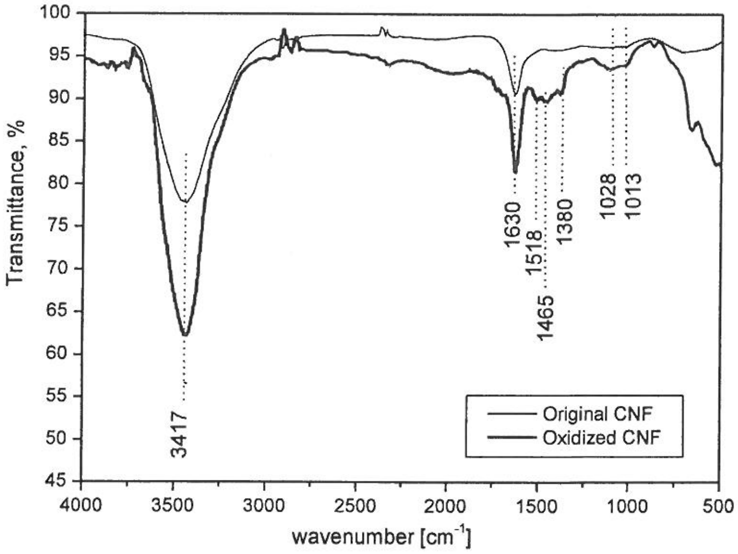

Figure 1: FTIR spectra of the oxidized and original carbon nanofibers.

Figure 2 shows the FESEM of the original and oxidized CNFs for two different magnifications respectively. It is reported that oxidation with concentrated acid is an effective way to remove the amorphous carbon, carbon black and carbon particles introduced during their preparation process [22]. The FESEM images illustrate that the fibre diameter size distribution of the original CNFs is broad with some of agglomerations of small size nanocarbon fibers (Fig. 2a). The stacked cup structure is clearly shown at higher magnification (Fig 2b). However, after the acid treatment the agglomerations were disappeared and the fibre size was more uniform (Fig 2c). Figure 2b show some of the fibers are wrinkles indicating the fibers structures that are made of limited number of anchoring sites. This observation is in line with findings reported by Kandah et. al. [24] based on adsorption study of nickel using carbon nanotubes.

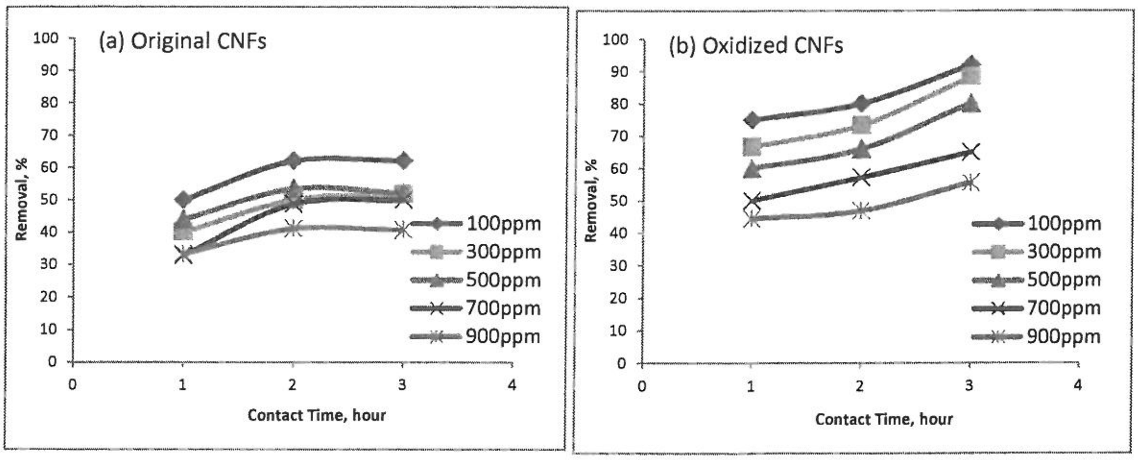

Figure 3: Effect of contact time on removal of nickel using (a) Original CNFs and (b) Oxidized CNFs. Initial metal concentration: between 100 mg/L to 900 mg/L; adsorbent dosage: 0.2 g/ 30 mL and pH: 7.

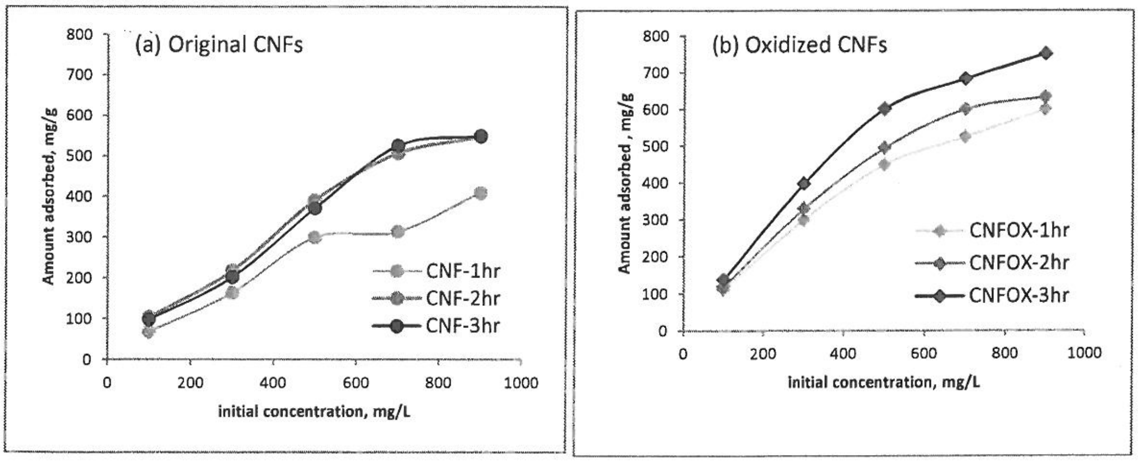

Figure 4: Effect of initial nickel concentration on the adsorption uptake of (a) Original and (b) Oxidized CNFs. Initial metal concentration: varies between 100 mg/L to 900 mg/L; adsorbent dosage: 0.2 g/ 30 mL and pH: 7.

Effect of initial concentration on the amount of nickel adsorbed on CNFs is shown in Figure 4. Increase the initial nickel ion concentration increases the amount of nickel ion adsorption capacity of both the adsorbents but the rate of the enhancement decreases as the initial is increased. The same nickel ion adsorption capacities of the original CNFs for the shaking periods of 2 and 3 hours at the same initial concentration suggests that the adsorption capacities for all the initial concentrations reach their maximum values in 2 hours. At low initial nickel (II)

Based on Langmuir model, the maximum adsorption capacity (q_m) varies from 1000 to 1400 mg/g for the original CNFs and from 1300 to 1700 mg/g for the oxidized CNFs. The adsorption of nickel ion capacity of the CNFs is enhanced by the acid treatment. Higher R^2 values (of between from 0.91 to 0.97) of the treated CNFs compared to those of the original ones indicates the Langmuir equation is better fit with the former. The critical characteristics of Langmuir model can be expressed in terms of its dimensionless separation factor or (R_L) which can be calculated using Eq. (4);

$$R_L = \frac{1}{(1+b\,C_o)} \tag{4}$$

where b is Langmuir constant and C_o is the initial concentration (mg/L). The R_L value indicates the nature of the adsorption: $R_L > 1$ (unfavorable), $R_L=1$ (linear), $0 < R_L < 1$ (favorable) or $R_L=0$ (irreversible). The R_L value for original CNFs is in the range of from 0.4 to 0.7 while for oxidized CNFs, the value lies from 0.1 to 0.2, meaning that the adsorption process is favourable for both adsorbents. Table 2 also shows the Freundlich isotherm constants. The closeness of the correlation coefficient (R^2) values of the adsorption data to one suggests that both the original and oxidized CNF adsorption fit well the Freundlich isotherm adsorption model. The n values of the Freundlich equation give an indication of the favorability of adsorption. Generally the value of n in the range of from 2 to 10 represents good, 1 to 2 is moderately difficult, and less than 1 denotes poor adsorption characteristics [29]. The values of n which are around 1.5 for the original CNFs and around 2 for the oxidized CNFs, indicate that adsorption for nickel ion are favorable for both adsorbents but as it is indicate in the Langmuir model, the acid treatment improves the nickel adsorption capacity of the CNFs.

Conclusion

The acid treatment significantly enhances nickel ion adsorption capacity of CNFs. The capacity to remove nickel (II) ion increases with the increment of contact time and initial concentration. The nickel ion adsorption by the original CNFs reaches the equilibrium in 2 hours but the adsorption capacity of the oxidized carbon nanofibers still increases further than this contact period. Although the nickel adsorption of both the original and modified CNFs fits into the Langmuir and Freundlich isotherm model, the analysis of the adsorption data shows that the modified CNFs is a better adsorbent than the original material. The FTIR spectra indicate that the acid modification increases the presence of oxygen functional groups on the CNF surface which consequently enhance the CNFs ability to adsorb nickel (II) ions.

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