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Removal of textile dyes by carbon nanotubes: A comparison between adsorption and UV assisted photocatalysis

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ABSTRACT

Amorphous carbon nanotubes were synthesized using low temperature solid state reaction. The as synthesized a-CNTs were used to remove two different textile dyes, Methyl Orange and Rhodamine B from water. Two ways of removal were followed; i.e. Adsorption and UV assisted catalysis. Adsorption experiment was carried out under various conditions. Analysis of the adsorption data was performed using Langmuir, Freundlich and Temkin models. It has been shown that the as prepared samples can effectively be used as adsorbent of textile dyes. Exposure of visible or UV light can make no significant additional effect to the removal efficiency.

The mechanism of the adsorption has been found to be following a pseudo 1st order mechanism with corresponding correlation factor >0.95. Also it has been shown that presence of impurities can drastically kill the performance of the sample. This detail comparative study has been reported for the first time.

1. Introduction

In the present era, textile industry is one of the most flourishing industry in India as well as world-wide. The most inevitable technology that is associated with textile industry is the process of dyeing where a very large amount of water is required. The requirement is mainly due to the need of cleaning excess dyes that remained unused and other auxiliary chemicals. It is estimated that approximately 10–50% [1] of the dyes used in the dyeing process is lost, and end up in the effluent.

Water pollution now becomes one of the major problems in India as well as throughout the world. A numbers of people throughout the world especially in third world countries like part of Asia and Africa are very much struggling to get pollution free hygienic water both for drinking as well as for house hold use. This creates the need for developing new means to provide clean water at affordable price.

The dyes, mentioned before end up in the water bodies due to the use of the activated sludge treatment in the effluent treatment plants, which have been shown to be ineffective in removing the toxicity and coloring of some types of dye.

The dyes are generally very stable compounds and thus are very much difficult to make them removed from the environment as well as make them free from toxicity. This inherent toxicity of these dyes is due to the basic demands of the associated industries, i.e. the dye should resist the biodegradation giving long term durability.

The different techniques that are used for other industry waste management are not very much suitable for tackling these textile dyes. Also at the same time the monotonous ingestion of water rich with textile effluents are constantly mixing with regularly usable pond and river water. This mixing up is thus causing serious damage to the human and other living orgasms due to toxicity, highlighting meta-genicity of its components [2]. Thus there are needs for developing suitable techniques like adsorption, ozonation, membrane separation, chemical oxidation-reduction, catalysis or other for efficient removal of these dyes.

Of these various techniques, adsorption finds extra attention due to its simplicity and effectiveness. Especially with the advent of nanotechnology and corresponding milestone discovery of carbon nanotubes (CNTs) and graphene has given carbon based nanotechnology a special importance in the field of adsorption technology. Even far before of this era, activated carbon like charcoal has got attention of the technicians and researchers as an effective remover of selective materials. Apart from textile dyes, these carbon nanostructures are suitable for removal of the heavy metals like lead, arsenic, chromium and others. However these techniques have limitations following the fact that due to the inert nature and high hydrophobicity of the material they are very difficult to disperse

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uniformly in water as well as in other polar liquids. Also the filtration process is time consuming and it is found difficult to regenerate and reuse of the material [3].

The carbon related nanostructures are mainly lacking their commercialization due to its complex synthesis procedure and low yield. Thus from this point of view amorphous analogue of CNT (a-CNTs) that are synthesized very easily with high yield can be the most effective alternatives. This a-CNT has further advantage over crystalline one regarding the fact that due to presence of large numbers of defects and more numbers of dangling bonds they are very easy to disperse in liquids and even without being externally functionalized by normal acid treatments or other. In our previous work, we have reported the adsorption efficiency of a-CNTs for removing the different dyes from water [4]. The material has shown its potential as remover of dyes from water. However, it should be noted that there is another very effective means of removing dyes from water that is photo assisted catalysis either in visible range or in UV range. There are reports of photo-catalysis assisted removal of dyes by CNT based hybrids however pure CNT does not show effective photo-catalysis. Thus it would be a good effort if one compares the dye removal efficiency of a-CNTs between two standard processes adsorption and photo-catalysis. Also the effect of iron oxide present in the sample, as the inevitable part of synthesis, on removal of dyes would be another study of interest. The last part is interesting as there are lots of report of iron oxide mediated removal of dyes from water [5].

Keeping this in mind this work reports the removal of dyes by chemically synthesized a-CNTs in presence and absence of external perturbations like UV excitation, impurities etc. Two types of dyes were taken and they are Rhodamine B (Rh-B; cationic) and methyl orange (MO; anionic). Different adsorption parameters like contact time, pH, dosage etc. are taken into consideration to see their effect on the removal efficiency.

Also a detail comparison has been between the process of pure adsorption and UV-assisted photo-catalytic removal of dyes. The experimental data have been well correlated with classical Langmuir-Freundlich, Temkin and Freundlich adsorption models.

2. Experimental

The synthesis of a-CNTs was done using a low term temperature, cost effective process reported in our previous work [6]. Briefly, Ferrocene and ammonium chloride (analytically pure) were taken in a weight ratio 2:1 and grounded finely in a mortar. The mixture was emptied in a Borosil glass beaker with proper covering so as to avoid instantaneous evaporation of ferrocene while heating. The mixture was then heated in a furnace at 250 °C for 30 min followed by natural cooling. The as obtained black powder was divided into two parts. For the first part the sample was consecutively washed with diluted HCl and de-ionized water in order to complete removal of trace amount of iron impurities (Sample A) whereas for the second part the sample is washed with de-ionized water (Sample B). In both the cases the sample was filtered and the final product was obtained only after drying the residue overnight in an oven at 80 °C.

All the as prepared samples were characterized by X-ray diffraction (XRD, Bruker), Field emission scanning electron microscope (FESEM, Hitachi, s-4800), transmission electron microscopy (HRTEM, JEOL-JEM 2100) and Fourier transform infrared spectroscopy (FTIR, Shinadzu 8400s), UV–Vis spectrometer (JASCO-V750).

Adsorption study has been done in the following manner:

The two dyes are taken in the purest form where stock solutions were made by using 0.4 g of each dyes in certain amount of deionized water. The working solution for each dye was prepared accordingly by diluting the stock solution.

For studying the effects of different sorption parameters like, dosage, contact time, and pH under normal light and UV irradiation, batch adsorption experiments were conducted at room temperature.

Two working solutions were prepared for two different dyes. For Rh B, 80 ml solution with concentration of 4.79 mg/L was prepared and for MO the corresponding value was 3.27 mg/L. In typical experiment, certain amount of a-CNTs were added into the solution and stirred for certain stipulated time. The solution was filtered time to time and the corresponding filtrate was taken out for UV–Vis spectroscopic study where the relative intensity determines the presence of relative amounts [For MO and RhB, the corresponding wavelengths are at 464 and 554 nm respectively] of dyes. The aforementioned experiment was also repeated under ultra violet irradiation.

The performance of the material as removal is measured in terms of removal efficiency (η) defined as

$$(\eta\ \%) = \frac{Co - Ce}{Co} \text{ x } 100 \quad (1)$$

The concentration of the adsorbed dye at time t i.e., Q_t and at equilibrium time i.e., Q_e were calculated according to the relations:

$$Q_e = \frac{Co - Ce}{m} \times V \quad (2)$$

$$Q_t = \frac{Co - Ct}{m} \times \text{V} \quad (3)$$

C_o and C_e are the initial and equilibrium concentrations of the dye (mg/ml) respectively, C_t is the dye concentration at time t, V is the volume of the solution (ml) and m is the amount of a-CNT (gm).

3. Results

3.1. XRD and microscopic analysis

Fig. 1 shows the XRD pattern of both sample A and B taken using Cu Kα radiation (wavelength λ = 0.15418 nm) with normal θ-2θ scanning in the range between 10 and 70°. It can be seen that there are differences in the spectra of sample A and B. However, both the sample show a weak peak centering around 2θ ≈ 26.5° which is the signature of the (002) plane of 2 dimensional graphitic phase of carbon [7]. Also it is seen that the two peaks are not very intense suggesting the poor crystallinity of the sample i.e. the as synthesized samples are defect rich. It is to be noted that the word amorphous CNT means CNT with less crystallinity. It is not that a material with zero crystallinity as a, short range ordering is always present in the sample. Due to this short range ordering one can see a broad peak in the XRD spectra not a sharp one as expected from a pure graphitic sample.

It is noteworthy that the intensity of the (002) peak of the sample A is much higher compared to that of sample B suggesting higher purity of the

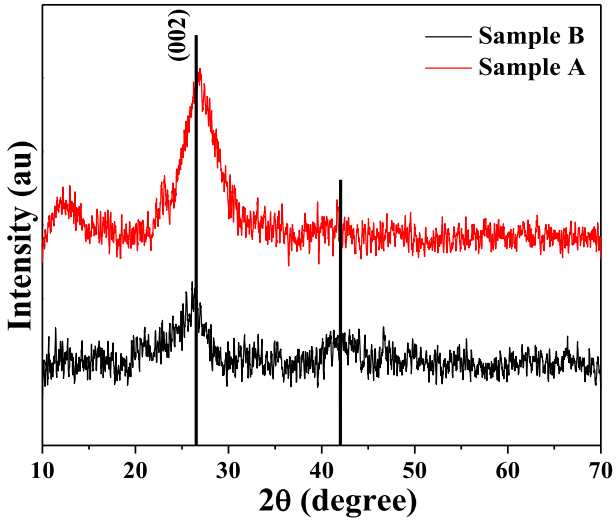

Fig. 1. XRD characteristics of both the sample A and B.