

## **REMOVAL OF PHENOL BY CARBON NANOTUBES AND ACTIVATED CARBON- A COMPARATIVE ANALYSIS**

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### **ABSTRACT**

Toxic organic substances are considered among the pollutants that have direct effect on humans and animals. Industrial wastewaters containing dissolved phenol compounds can contaminate groundwater resources and thus lead to a serious groundwater pollution problem. In the present research, the adsorption technique for the efficient removal of organic substances at trace level was employed. It is a mass transfer process that involves contact of a solid (adsorbent) with a fluid containing the target solute (adsorbate). Carbonaceous materials such as carbon nanotube (CNT) and activated carbon (AC) are characterized by their extraordinary large specific surface area, well-developed porosity and tunable surface-containing functional groups. As a result, these carbon materials were utilized in this study as adsorbents for the removal of phenol compounds from synthetic contaminated water. Four parameters including pH (2-7) of the solution, agitation speed (50-250 rpm), contact time (0-12 hr), and adsorbent dosage (0-500 mg) were varied in order to determine their influence on the removal of phenolic compounds from water and to investigate the influence of these parameters on the adsorption rate. The concentration of phenol in water before and after treatment was analyzed using UV-Spectroscopy.

### **1. INTRODUCTION**

Environmental pollution is currently one of the most important issues facing humanity. It has increased exponentially in the past few years and reached alarming level in terms of its effects on living creatures. Toxic organic substances are considered one of the pollutants that have direct effect on man and animals. Industrial wastewaters containing dissolved polycyclic aromatic hydrocarbons (PAHs) and phenols, for example, can contaminate groundwater resources and thus lead to a serious groundwater pollution problem. Exposure to such chemicals can damage the central nervous system, respiratory system, kidney, and blood system if entered into human body [1]. Moreover, some of PAHs may reasonably be expected to be carcinogens. Industrial wastewater contaminating materials such as Volatile Organic Compounds (VOCs), Polychlorinated Biphenyls (PCBs) and PAHs are mainly generated from the petroleum and petrochemical industries. Some of them are produced by fires, as well as, in the exhaust of generators

and motor vehicles. It is estimated that 30% of the amount of PCBs produced in EU, for example, are spilled into the environment [2]. In Russia, recent statistics showed that 13 million people are in contact with organic compounds such as phenols where the world's largest aluminum and steel plants are located. Moreover, Benzopyrene content is monitored in 170 Russian cities where there is a great number of small coal-powered boiler houses that create a stable seasonal pollution at a rather high level of  $>3 \text{ ng/m}^3$  [3]. In Arab countries, the situation is similar where many countries do not control release of persisting organic compounds, or fail to implement existing legislation. These problems are often compounded by the lack of treatment, unsafe transport, concentration in urban areas and inadequate management [4]. Agency for Toxic Substances & Disease Registry, USA, has classified phenols as the top 45<sup>th</sup> priority hazardous substances, that need urgent treatment before entering into the environment [5]. Therefore, removing these organics or decreasing their concentrations to the permitted levels before discharging becomes a challenging issue. Several technological processes can be performed to remediate organic compounds from water. Bioremediation of phenols and low molecular weight PAH is a preferred technique because of its ease of implementation but tends to be timely and often incomplete especially at high-molecular weight PAHs (with five or six aromatic rings), which are proven to be more recalcitrant to biological degradation [6]. Transformation/mineralization of these contaminants using ultraviolet (UV) radiation is also efficient, however, it can be costly particularly at a large scale [6-7]. Oxidation using ozone, hydrogen peroxide, permanganate or persulfate, as well as, advanced oxidation techniques (AOTs) using Fenton's reagent, activated persulfate and perozone are efficient to even most intractable organic compounds; however, for groundwater applications only certain AOTs are applicable [8].

Other physical and chemical remediation techniques applied to contaminated soil is venting using solvents and surfactants. The limitation to this technique is the requirement of high solvent concentrations that are needed to achieve good results [9].

Adsorption can be employed efficiently for removal of organics at trace level with low cost. It is a mass transfer process that involves contact of a solid (adsorbent) with a fluid containing the target solute (adsorbate). The surface area of the adsorbent generally governs adsorption efficiency and selectivity as a result of accumulation of the adsorbate on the surface of the adsorbent. Among the potential adsorbent materials are carbon-based compounds which are hydrophobic and non-polar, including materials such as carbon nanotube (CNT) and activated carbon (AC). Carbonaceous materials such as CNT and AC are characterized by their extraordinary large specific surface area, well-developed porosity and tunable surface-containing functional groups. As a result, these materials are widely used as adsorbents for the removal of solutes/pollutants from water and wastewater [10-12]. Activated carbon in particular is extensively used for removal of both organic and inorganic compounds from aqueous solution. CNT, on the other hand, has recently been utilized for removal of heavy metals from solution. However, little information is available in literature regarding its capacity to remove organics from liquid medium.

In this paper, both CNT and AC materials were utilized to investigate their removal efficiency of phenol from contaminated water.

## **2. EXPERIMENTAL METHODOLOGY**

Batch mode adsorption experiments were conducted at room temperature to study the effect of initial solution pH, agitation speed, contact time, CNTs and AC dosage on the adsorption of phenol (organic pollutant). Multi-walled carbon nanotube (MWCNT) with 10-20 nm diameter, 5-15  $\mu\text{m}$  length,  $\geq 95\%$  purity, were utilized. The phenol concentration in the initial solution was kept constant at 1 mg/L. Each experiment was conducted in volumetric flask and the initial and final concentrations of phenol were analyzed using UV spectroscopy.

## **3. RESULTS DISCUSSION**

### **3.1 Effect of pH on removal**

The variation of pH used in the experiments was within the range of 3 to 9. The following parameters were kept constant namely, contact time of 2 hr, dosage of adsorbent of 50 mg, and shaking speed of 100 rpm. The results obtained by varying the pH on the removal of phenol in water solutions containing CNTs, and AC adsorbents are shown in Figure 1. The pH was found to be a predominant factor affecting the removal of phenol under the studied conditions. It was noticed that with increasing pH from 3 to 7 the removal of phenol in the solution, by CNTs and AC, increased continuously and then decreased within the pH range of 7-9. It is worth mentioning that the removal was very low for phenol, for these two adsorbents, at pH level below 3. At pH 7 the maximum percentage removals of phenol, by CNTs and AC, were found to be approximately 50% and 65%, respectively. Based on these results, pH value of 7 was kept constant in the subsequent experiments in which the effects of agitation speed; contact time and dosage amount of adsorbent were investigated. Overall, AC exhibits a slightly higher removal compared to CNT. The difference in adsorption capacity of CNTs and AC at different pH may be due to the difference in the concentrations of  $\text{H}^+$  and  $\text{OH}^-$  in the solutions. Adsorbent particles have active sites with negative charges. The  $\text{H}^+$  ions within low pH environments can neutralize those negative particles, reduce the hindrance to diffusion of phenol ions and consequently increase the chances of their adsorption. High pH environments led to high concentration of  $\text{OH}^-$ , which can increase the hindrance to the diffusion of phenol ions and thus reduce the chances of their adsorption.

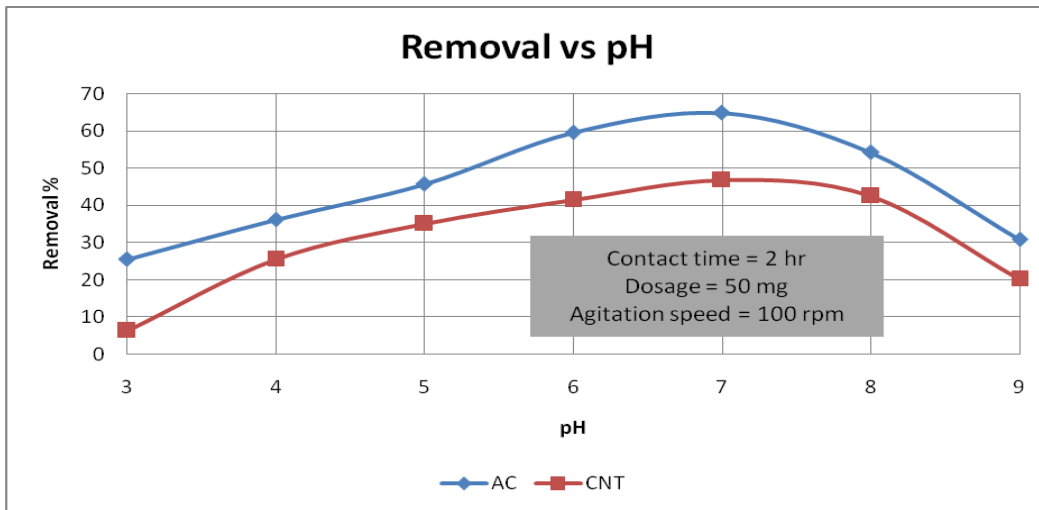


Figure 1: Removal of phenol versus pH for both CNT and AC containing water solutions

### 3.2 Effect of agitation speed

The peak removal obtained above at pH 7 was used to study the effect of the agitation speed on adsorption capacity of phenol by the two adsorbents, CNT and AC. Moreover, the following parameters were kept constant namely, contact time of 2 hr, and adsorbent dosage of 50 mg. By varying the speed of agitation from 50 to 250 rpm as shown in Figure 2, it was observed that the percentage of phenol removal increased with increasing speed up to the agitation speed of 150 rpm for both adsorbents, then the adsorption rate remained constant afterwards. It is clear that agitation facilitates proper contact between the ions in solution and the adsorbents binding sites and thereby promotes effective transfer of phenol ions to the carbon active sites and improves the diffusion of phenol towards the surface of the CNT and AC adsorbents.

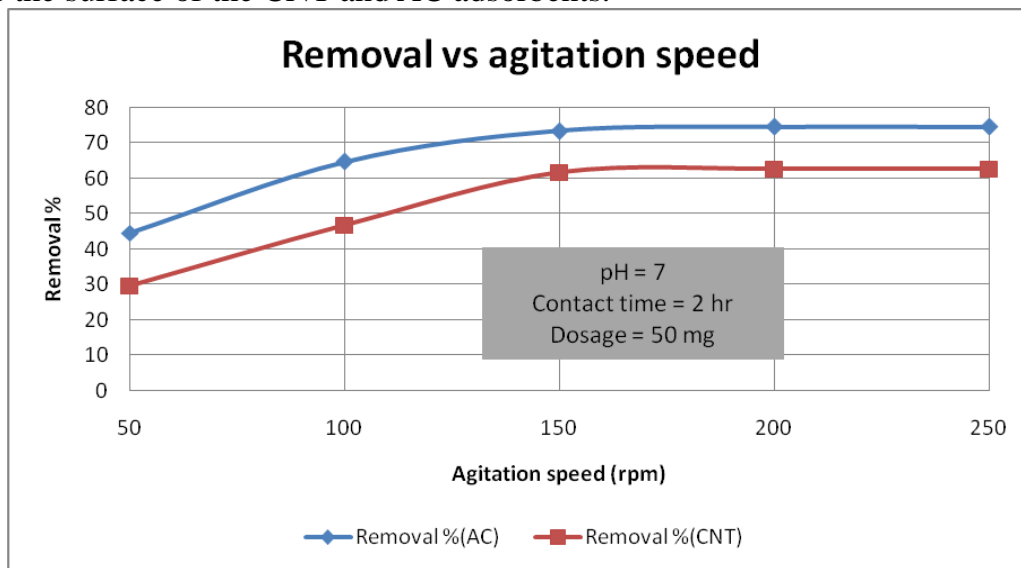


Figure 2: Removal of phenol versus agitation speed for CNT and AC adsorbents

### 3.3 Effect of contact time

The adsorption behavior of phenol by the two considered adsorbents as a function of contact time was studied by varying the contact time from 10 minutes to 12 hours at a phenol concentration of 1 mg/L, a dose of adsorbent of 50mg/L, and pH of 7. The agitation speed was fixed at 200 rpm throughout the experiments. The results presented in Figure 3 show that, the adsorption rate reached the equilibrium for both adsorbents after two hours and the removal rates of phenol were about 65% and 75% for CNTs and AC respectively. A slight drop in the removal percentage was obtained beyond two hours contact time.

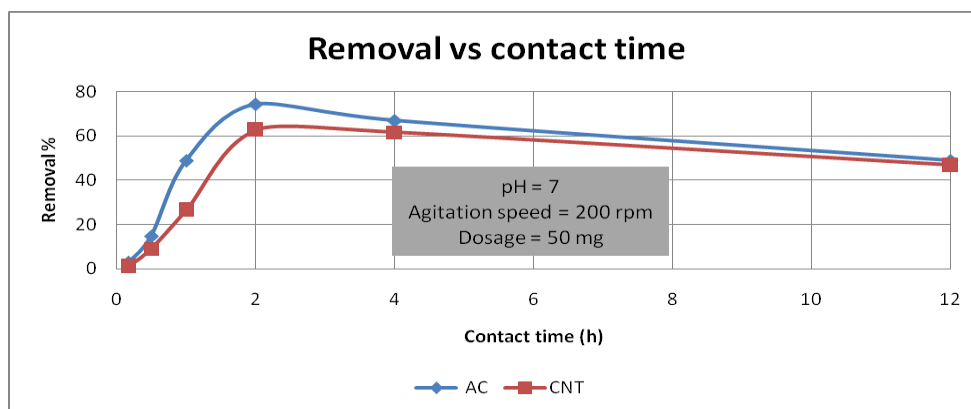


Figure 3: Removal of phenol versus contact time for CNT and AC adsorbents

### 4. EFFECT OF DOSAGE

The amount of adsorbents in the water is one of the major factors, which affects the adsorption capacity. The batch adsorption experiments were carried out using various amounts of CNTs and AC from 25 to 500 mg while the pH, agitation speed and contact time were fixed at 7, 200 rpm and 120 minutes, respectively. The results displayed in Figure 4 indicate that the adsorption capacity increases with increase in adsorbent dosage up to 400 mg, then remains almost constant for the remaining dosage range. For the range below 400 mg, the increase in percentage removal with the increase in dosage rate is expected because the higher the dose of adsorbents in the solution, the greater the availability of exchangeable sites for ions. However, after certain dosage rate, which is 400 mg in this study, the dosage rate was found to have no effect on the percentage removal. This would indicate that the phenol removal is an equilibrium reaction and is not limited by number of adsorption sites of the adsorbent within the concentration range investigated in this study.

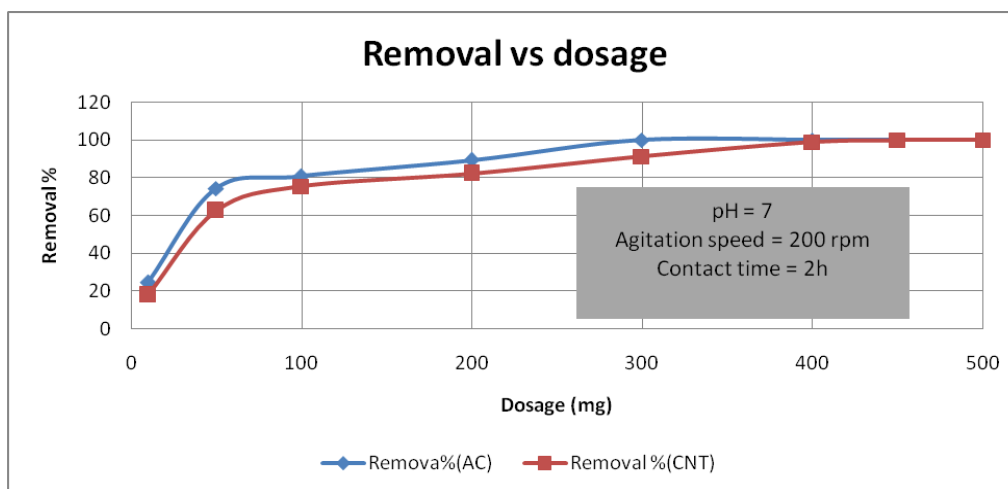


Figure 4: Removal of phenol versus dosage of CNT and AC adsorbents

## 5. CONCLUSIONS

In the present study, the influence of four parameters namely pH of the solution, agitation speed, contact time, and adsorbent dosage (CNT and AC) were investigated to determine their influence on the removal of phenolic compounds from water. It was noticed that with increasing pH from 3 to 7 the removal of phenol in the solution increased continuously and then decreased within the pH range of 7-9. At pH 7 the maximum percentage removals of phenol, by CNTs and AC, were found to be approximately 50% and 65%, respectively.

With regard to agitation speed, the percentage of phenol removal increased with increasing speed up to 150 rpm for both adsorbents, then the adsorption rate remained constant afterwards. Agitation facilitates proper contact between the ions in solution and the adsorbents binding sites thereby promoting effective transfer of phenol ions to the carbon active sites in CNT and AC adsorbents.

For the contact time, the adsorption rate reached equilibrium for both adsorbents after two hours and the removal rates of phenol were about 65% and 75% for CNTs and AC respectively. A slight drop in the removal percentage was obtained beyond two hours contact time.

Finally, the adsorption capacity increased with increase in adsorbent dosage up to 400 mg, then remains almost constant for the remaining dosage range.

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## REFERENCES

- [1] EPA, EPA National Library Network. U.S. Environmental Protection Agency, URL: <http://www.epa.gov/natlibra/ols.htm>: 2007.
- [2] CEC, C. O. T. E. C. *Community Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants*; Brussels, 2007.
- [3] Kurlyandsky, B. *Top-Rated Pollutants in Russian Federation*; United Nations Environment Programme: St. Petersburg, Russian Federation, 1997.
- [4] BCRC-Cairo *Regional Workshop for Arab States on the Environmentally Sound Destruction of POP and Decontamination of POP Containing Waste in the Context of Basel Convention and Stockholm Convention*; Amman, Jordan, 2005.
- [5] ATSDR, CERCLA Priority List of Hazardous Substances. Department of Health and Human Services, USA. URL: <http://www.atsdr.cdc.gov/cercla/05list.html>: 2007.
- [6] Alderman, N. S.; Guessan, A. L. N.; Nyman, M. C., Effective treatment of PAH contaminated Superfund site soil with the peroxy-acid process. *Journal of Hazardous Materials* 2007, *146*, 652-660.
- [7] Iuster-Teasley, S. L.; Yao, J. J.; Herner, H. H.; Trosko, J. E.; Masten, S. J., Ozonation of chrysene: evaluation of byproduct mixtures and identification of toxic constituents. *Environ. Sci. Technol.* 2002, *36*, 869-876; Tuhkanen, T. A.; Beltran, F. J., Intermediates of the oxidation of naphthalene in water with the combination of hydrogen peroxide and UV radiation. *Chemosphere* 1995, *30*, 1463-1475.
- [8] EPA, *Advanced Photochemical Oxidation Processes*. U.S. Environmental Protection Agency: Washington, DC, 1998.
- [9] Antizar-Ladislao, B.; Lopez-Real, J.; Beck, A. J., Laboratory studies of the remediation of polycyclic aromatic hydrocarbon contaminated soil by in vessel composting. *Waste Management* 2005, *25*, 281-289.
- [10] Hussain, C. M.; Saridara, C.; Mitra, S., Modifying the sorption properties of multi-walled carbon nanotubes via covalent functionalization. *Analyst* 2009, *134* (9), 1928.
- [11] Lu, C.; Liu, C.; Su, F., Sorption kinetics, thermodynamics and competition of Ni<sup>2+</sup> from aqueous solutions onto surface oxidized carbon nanotubes. *Desalination* 2009.
- [12] Shamspur, T.; Mostafavi, A., Application of modified multiwalled carbon nanotubes as a sorbent for simultaneous separation and preconcentration trace amounts of Au(III) and Mn(II). *Journal of Hazardous Materials* 2009, *168* (2-3), 1548.