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Effect of Electrolyte on Adsorption Behaviour on Graphene

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The effect of matrix on the adsorption of *p*-nitrophenol on graphene was studied. Six different salts (NaCl, CH_3COONa, Na_2SO_4, NaBr, NaSCN and Na_2CO_3) were added to the aqueous adsorption mixture with three different concentrations. The results showed the existence of four classifications for the salt effect on adsorption; adsorption promoters, adsorption inhibitors, salt independence and concentration dependence adsorption. Acetate and carbonate ions are considered as concentration dependent adsorption salt; high concentration of acetate inhibits the adsorption ability of graphene toward *p*-nitrophenol where high concentration carbonate shows an increase in the adsorption capacity. The effect will reverse at high concentration of acetate ion and carbonation. The results also showed that the adsorption of *p*-nitrophenol is highly sensitive to the medium acidity which controls the reversible phenol phenolate equilibrium. The ratio between the adsorption at highly acidic and highly basic media reaches more than 90 %. The adsorption isotherms for high concentration of sulfate solution, fitted by Langmuir and Freundlich models, showed an order of magnitude increase in the maximum adsorption capacity parameters as compared to the adsorption in pure aqueous medium.

Keywords: 4-Nitrophenol, Sulfate, Acetate, Carbonate, Acidity, Graphene.

INTRODUCTION

One layer of the graphite, a planar arrangement of benzene rings, is considered to be the thinnest material that has been detected on earth. Due to its unique dimensions and characteristics; it is projected that graphene will soon enter in every field in our life. Recent experiments on the adsorption of graphene from aqueous forms were carried on toward several pollutants such as phosphate [1], methyl orange [2], acrylonitrile, *p*-toluenesulfonic acid, 1- naphthalenesulfonic acid and methyl blue [3]. Also, adsorption of methylene blue [4] and bisphenol-A (BPA) on graphene from aqueous solution [5]. These studies show promising results especially in case of existing of benzene ring in the structure of the pollutant and can be extended to other more hazardous materials.

Long-term exposure to *p*-nitrophenol at work has been associated with cardiovascular disease. Also, ingestion of liquid products containing concentrated *p*-nitrophenol can cause serious gastrointestinal damage and even death. Severe skin damage can be expected from applying *p*-nitrophenol to skin [6]. Nitrophenols can enter our body through breathe, swallow, or even touching their sources. Nitrophenols can be found in air and rainwater [7].

The study of the adsorption of *p*-nitrophenol on graphene is beneficial for two reasons; firstly it is considered to be among the hazardous materials, *p*-nitrophenol LD_{50} for rats equal to 250 mg/kg [8]. So there is urgent need to get rid of it especially from aqueous solutions and adsorption on a relatively cheap material (like graphene) will a good choice. Secondly, its importance in the catalysis field. The reduction of *p*-nitrophenol to *p*-aminophenol is usually used as a model reaction for measuring the activity of the catalytic processes. Several graphene based catalysts for *p*-nitrophenol/aminophenol conversion were made [4,9-11]. Among the most important steps of any heterogeneous catalytic process involves the adsorption and desorption steps. Several studies were done searching for a good adsorbents for the removal of 4-nitrophenol [12-20]. For example the adsorption of 4-nitrophenol was studied on activated charcoal [21] and by low cost calcium alginate clay composites [22].

We have done a study on the adsorption of *p*-nitrophenol on graphene from aqueous medium. The study took several factors that usually affect the adsorption as temperature, time interval and dosage amount of graphene. The objective of this study is to investigate the effect of salts and medium acidity on the adsorption ability and behaviour of graphene toward *p*-nitrophenol. Sodium chloride, sodium sulfate, sodium acetate, sodium carbonate, sodium bromide and sodium thiosulfate were used to investigate their effect on the adsorption capacity of graphene. In addition it includes the effect of salt concentration on the adsorption process.

EXPERIMENTAL

Extra pure and fully characterized graphene was purchased from Angstron Materials® Co. Ltd (N008-P-10 Polar Graphene, powder thickness = 50-100 nm and x-y dimensions is less or equal 5 μm). Highly pure *p*-nitrophenol, analytical grade HCl, NaOH, NaSCN, NaCl, Na_2CO_3, Na_2SO_4 and NaBr were purchased from Sigma Aldrich. Distilled deionized water was used for all experiments. All results are based on the average of at least three experiments.

Batch and salts experiments: The stock solution of *p*-nitrophenol (1000 mg/L) was prepared by dissolving *p*-nitrophenol in distilled deionized water and further diluted to the required concentration before used. All the experiments were done at room temperature due the fact our previous work showed that the adsorption of *p*-nitrophenol on graphene is an exothermic process. The effect of pH and salts were performed using the optimum conditions for adsorption Graphene weight = 0.09 g and *p*-nitrophenol solution will be added and diluted to make the final concentration is 10 mg L^{-1} and final volume is 100 mL. If sodium salt will be added, the specific amount of the interested salt will be added to make the desired concentration with taking care of the final concentration and volume of the adsorption solution. The mixture will be mixed in 250 mL reagent fitted bottles after sealed using parafilm. The reagent flasks were shaken at 900 rpm using a vibrator (HZQ-F160) on a water bath (GFL, Germany) for 24 h. After that the supernatant was filtered using double Whatman® filter papers (grade 42). The concentration of the adsorbed *p*-nitrophenol was determined from the absorbance of the solution before and after the adsorption process. Absorbance measurements were done after adding 5 μL of 1 M NaOH solution to the 2 mL absorbance-cuvette just before putting it into using a UV-visible spectrophotometer (Lambda 35, Perkin Elmer, USA). The above optimum conditions for adsorption and measurements were taken from previous study [23].

UV-visible spectrum of the *p*-nitrophenol at two different pH was done by adding small amount of conc. hydrochloric acid or sodium hydroxide to the *p*-nitrophenol solution (10 mg/L) to make the final pH either 3 or 9. The evaluation of the pH effect was carefully done by either adding hydrochloric acid (5 M) or sodium hydroxide (5 M) to the adsorption solution to make the pH at the desired acidity or basicity. The added volume of HCl or NaOH was less that will not affect the total volume of the adsorption solution. Finally, as mentioned above the measurements of the left over *p*-nitrophenol was done for the filtrate after adding 5 μL of 1 M NaOH solution to make the final solution basic so we can measure the predominant phenolate species that absorbs strongly at 400 nm.

The final *p*-nitrophenol concentrations of supernatants were determined by measuring the absorbance of the samples at the absorbance maximum wavelength of 400 nm by a UV-visible spectrophotometer. The uptake of the adsorbate at equilibrium, q_e (mg/g), was calculated by eqn. 1:

$$q_e = \left(\frac{C_0 - C_e}{m}\right)V \quad (1)$$

where C_0 and C_e were initial and equilibrium concentrations of *p*-nitrophenol (mg/L), respectively, m was the mass of adsorbent (g) and V was volume of the solution (L). Different time intervals were taken to measure the amount of uptake for the kinetic experiments. The effect of different dosage of graphene was studied.

RESULTS AND DISCUSSION

Adsorption behaviour

Effect of pH: *p*-Nitrophenol has a pka of around 7.1. Below this value it is expected to have *p*-nitrophenol as predominant species, whereas above this value, *p*-nitrophenolate (anion) is the predominant. The UV-visible spectrum of the *p*-nitrophenol at the acidic (pH ~ 3) and basic (pH ~ 9) solutions as is shown in Fig. 1. It seems from the spectra that measurements of *p*-nitrophenol is more convenient to be taken at alkaline condition because of the high absorption of the *p*-nitrophenolate species at 400 nm and almost no absorption of phenol form. Therefore, all UV visible measurements of the left over *p*-nitrophenol in solution was taken at pH > 9 by adding 5 μL of concentrated NaOH to the UV-visible cuvette (total volume of 2 mL).

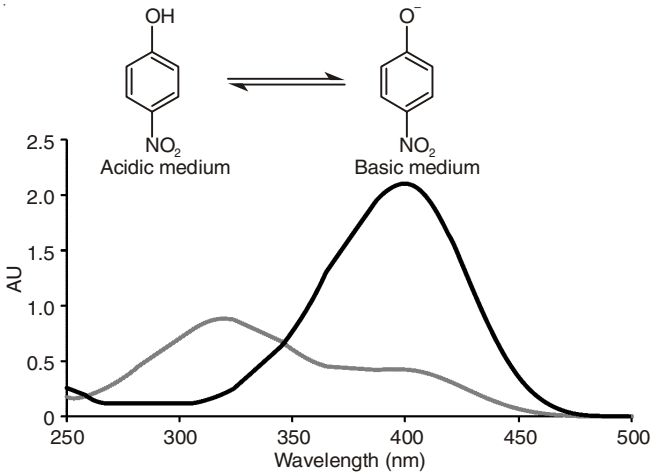

Fig. 1. UV-visible absorption spectra of *p*-nitrophenol on acidic and basic media. The change in the spectra is due to the equilibrium between the *p*-nitrophenol and *p*-nitrophenolate ion with changing the pH of the solution (This curve was taken from the reference [23])

The effect of acidity on the adsorption of *p*-nitrophenol on graphene was illustrated (Fig. 2) in which same initial concentration of *p*-nitrophenol on graphene was used at different pH's. The adsorption is highly dependence on the pH of the solution. Two main regions can be distinguished; low pH region (< 6) and high pH region (> 10). This could be a very strong evidence that the adsorption carried out predominantly for the phenol form and in very low extent to the phenolate species. In light of the above facts about pH effect; the adsorption of *p*-nitrophenol has to be done at low pH (5-6) and the measurements of the left over *p*-nitrophenol has to be measured at high pH (> 9) at λ = 400 nm. This will ensure the adsorption of the high probable species (phenol form) and accurately measure remaining *p*-nitrophenol by converting it to phenolate form.

Effect of salts: Changing the general electrolyte of the solution was done by changing the matrix salt. The initial concentration of *p*-nitrophenol was fixed to be 11.1 mg g^{-1}

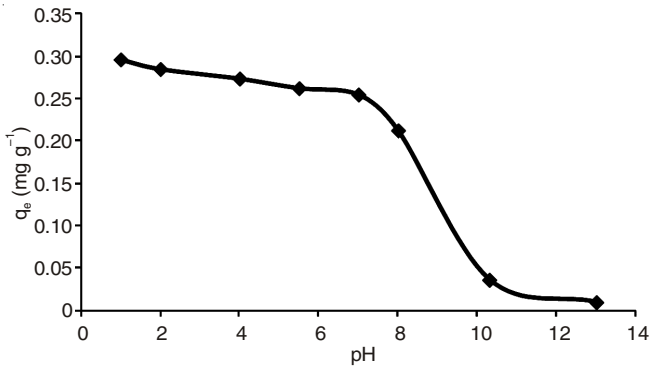

Fig. 2. pH effect on the adsorption of *p*-nitrophenol onto graphene. The adsorption uptake was taken at different pH value for 24 h of shaken at 298 K

due to the fact that this value shows a good adsorption capacity and good adsorption removal rate at the same time. [23] The results of effect of salts are shown in Fig. 3, where the relative adsorption is calculated by subtracting the adsorption of *p*-nitrophenol in pure water from the adsorption that happens when adding the salt.

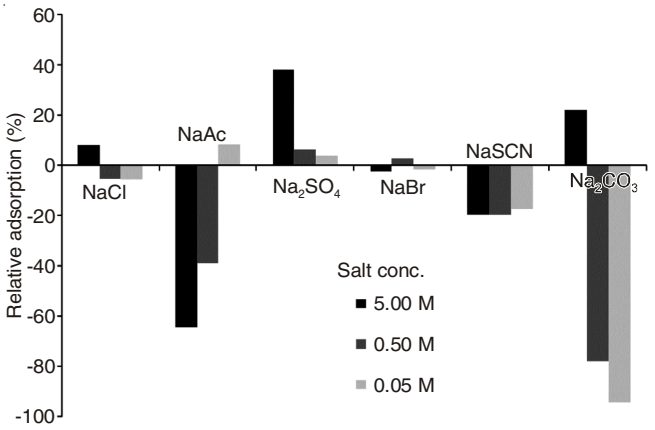

Fig. 3. Effect of salts on the adsorption of *p*-nitrophenol referenced with the doubly deionized water solution. The relative adsorption was calculated as the difference of the adsorption of *p*-nitrophenol in presence and absence of salts. Changing the concentration of the salt on the adsorption process is also demonstrated

Sodium bromide shows almost no difference on the adsorption of *p*-nitrophenol at all concentrations. Sodium chloride appears to have little change on the adsorption process. Sodium thiosulfate inhibits the adsorption process by about 20 % with no concentration effect. Acetate and carbonate are considered basic and acid salts respectively. This may explain their effect on the adsorption process due to the change on the reversibility and availability of the phenol form that is responsible for the adsorption. High concentration of sodium acetate as well as low concentration of sodium carbonate almost completely inhibit the adsorption of *p*-nitrophenol. Sodium acetate and sodium carbonate seem to flip the effect with concentration; low concentration of sodium acetate and high concentration of sodium carbonate promotes the adsorption of *p*-nitrophenol on graphene. High concentration sodium sulfate was highly preferable for the adsorption process with an increase of more than 40 %. As the concentration of sodium sulfate increases the increase on the adsorption occurred, but with less extent.

It is believed that changing of electrolyte of the matrix may be due to the polarization and the availability of the phenol form of the *p*-nitrophenol. The NO_2 and OH groups on the *p*-nitrophenol may probably carry a relatively major role on the adsorption process of *p*-nitrophenol on graphene. The results of this study are in disagreement with a theoretical study carried by Humpola *et al.* [24] that claimed that the adsorption is highly independence on the medium due to their finding of having π-π interactions to be the dominant forces in the adsorption process of phenol compounds on graphene.

Langmuir fitting: We have tried to study the adsorption behaviour of *p*-nitrophenol at different dosage of graphene with the existence of salts at different concentrations. However only high concentration sodium sulfate solution provides a reasonable and reproducible adsorption isotherm. Other salts and low concentration of sodium sulfate shows a large error bars especially at low graphene concentration (where the Langmuir and Freundlich models fits the best). Fig. 4 shows the isotherms of *p*-nitrophenol on graphene with and without sodium sulfate. The results were fitted against both Langmuir and Freundlich models (eqns. 2 and 3). The Langmuir model assumes that a monolayer adsorption of *p*-nitrophenol occurs on a homogenous surface. It also suggests that there is adsorption without interaction between the adsorbate and the adsorbed species. The equation for Langmuir model is:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max} k_L} \quad (2)$$

where q_{max} is the maximum adsorption capacity (mg/g). Also, k_L is a parameter that is related to the energy of adsorption (L/mg) that characterizes the affinity of the adsorbate to the adsorbed species. q_{max} and k_L can be determined from the plot of C_e/q_e against C_e. The linear form of the equation used for the Freundlich model can be written as follows:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (3)$$

where k_F and n are adsorption capacity and the adsorption intensity, respectively. Both of them are considered as a

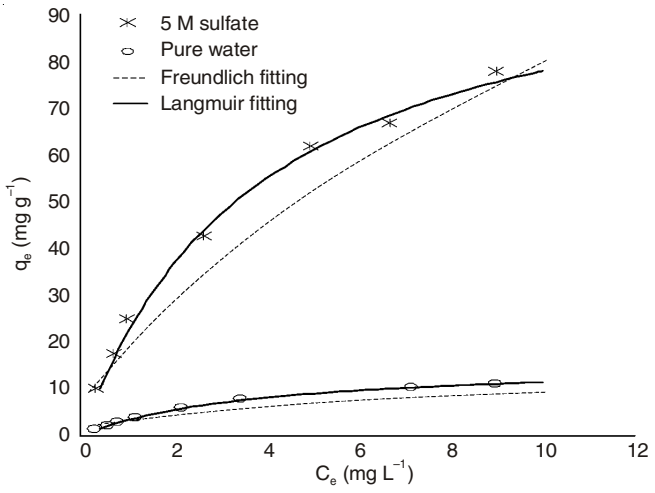

Fig. 4. Langmuir fittings of the adsorption of *p*-nitrophenol on graphene from a high concentration sodium sulfate and sodium chloride solutions (5 M concentration) as compared with the previously published study carried on in pure water (distilled deionized water) [23]. The initial concentration of *p*-nitrophenol is 11.1 mg/g

TABLE-1
LANGMUIR AND FREUNDLICH BEST FIT PARAMETERS FOR THE ADSORPTION OF *p*-NITROPHENOL IN 5 M Na_2SO_4 SOLUTION COMPARED TO THE PURE WATER STUDY (Ref. [23]). THE ADSORPTION OF *p*-NITROPHENOL ON GRAPHENE HAD BEEN PERFORMED AT ROOM TEMPERATURE (298 K) AT pH = 6

	Langmuir			Freundlich		
	q_{max}	k_L	r^2	1/n	K_F	r^2
Pure water (Ref. [23])	15.5	0.27	0.999	0.45	3.38	0.970
Na_2SO_4	108.1	0.26	0.987	0.56	23.9	0.973

characteristic parameters for the adsorption system that are obtained by plotting ln q_e against ln C_e. The final results of the Langmuir and Freundlich parameters of the adsorption of *p*-nitrophenol on graphene with and without the addition of sulfate are summarized in Table-1.

Sodium sulfate shows an order of magnitude increase in the maximum adsorption capacity and adsorption capacity (q_{max} from the Langmuir fitting and K_F from Freundlich fitting) of *p*-nitrophenol on graphene. Other parameters were almost the same; k_L from Langmuir and 1/n from Freundlich fittings which probably means that the addition of sulfate does not change the thermodynamic properties of the adsorption process as a whole.

Conclusion

The adsorption of *p*-nitrophenol on graphene was studied under extreme condition of low to very high concentration of salts. Sodium sulfate is considered among the adsorption promoters whereas high concentration of sodium acetate and low concentration of sodium carbonate were considered inhibitors. Salts like sodium chloride and sodium bromide have almost no significant change on the adsorption. The results also showed that the adsorption of *p*-nitrophenol is highly sensitive on the medium acidity. The adsorption isotherms for high concentration of sodium sulfate solution showed an order of magnitude increase the adsorption capacity as compared to the adsorption in pure aqueous medium.

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