Removal of Naphthalene and Anthracene from Surface Water of Hyderabad Using Graphene Oxide

Munir Abbas[1], K.M.Brohi[1], Rafi-uz- Zaman[1], Nanik Nandaani[1]

[1] *Institute of Environmental Engineering and Management, Mehran-UET Jamshoro.*

***Abstract*: In Pakistan, surface water (rivers lakes, canals ponds, and canals) is mostly used for the domestic, industrial and irrigation purposes. Polyaromatic hydrocarbons (PAHs) are family of organic compounds having benzene rings in their structure, which can affect human health as well as aquatic species. In this study, naphthalene(C10H8) and anthracene(C14H10) which are two basic compounds of poly aromatic hydrocarbons family (PAHs), have been assessed and removed from the surface water of Hyderabad using graphene oxide as the adsorbent, graphene oxide was prepared manually from graphite through Hammer`s method in the water quality laboratory at Institute of Environmental Engineering and Management (IEEM). Prepared adsorbent is characterized by SEM (scanning electron microscopy) and Dynamic light scattering (DLS) techniques. UV-spectrophotometer is used to analyze the synthetically made samples. Different Parameters for removing of naphthalene and anthracene from surface water have been investigated, such as; pH, adsorbent dosage, contact time, and concentration of the contaminants. Results of this study showed that highest removal efficiency of Graphene oxide (GO) for naphthalene was observed as 93.16% by using 300mg of GO dosage at pH 2, reaction time of 120 minutes, and 20ppm concentration, and to remove anthracene from surface water the maximum efficiency was noted as 95% at pH 5, GO dosage 300mg, contact time 90 minutes in 20ppm concentration. Adsorption data is analyzed by Langmuir and Freundlich isotherm models.**

***Keywords*: Adsorption, Anthracene, Graphene Oxide, Naphthalene, Polyaromatic Hydrocarbons (Pahs).**

I. INTRODUCTION

In Pakistan around 72% of drinking water is obtained from aquifers, water policy developed in 2018 by ministry of water resources government of Pakistan aimed to provide uncontaminated drinking water to all people of Pakistan by the year 2025 by eliminating the contaminations and impurities in water and treating the water with reliable technologies to minimize the ratio of water borne diseases among the people [1]**.** Naphthalene and Anthracene are two toxic compounds of PAHs family having two and three rings of carbon and hydrogen atoms in their structure respectively. Under usual conditions naphthalene is white to light brown solid or powder form flammable compound which has strong distinctive smell but not unpleasant [2] whereas anthracene is a white to yellowish solid with weak smell, molecular weight of naphthalene is 128.9 g/mol and anthracene has molecular weight of 178.2 g/mol, both do not dissolve in water [3]. Naphthalene and anthracene are naturally present in fossil fuel so they are released in environment when it burns [4] other causes of increase in presence of PAHs in environment include forest fire, volcanic eruption, cigarettes smoke, vehicle exhaust and industrial effluent [5].

Main source of presence of these two PAHs in water usually develops through thick coating of coal tar on pipes which are used to distribute water within cities and surrounding areas, this coating is done in order to protect pipes from rust and corrosion [6]. In developing countries there is higher level of contamination of drinking water by coal tar coating of pipes [7]. Surface water polluted with PAHs is arising as burning issue especially in areas where surface water is being used for most of domestic chores in big cities of Pakistan like Karachi, Lahore, Faisalabad, Gujranwala, Hyderabad and Islamabad. In cities people mainly receive water through water supply which is dependent on nearby rivers or canals connected to that city in order to provide water to its residents for domestic purposes and for industrial sector also, the elevated levels of PAHs have been noticed in many regions of Pakistan in recent years. In 2014 study was carried out to analyze the presence, circulation and resources of Σ17 PAHs in Soan river, it was noted that PAHs of low molecular weight were greater (65%) in concentration than PAHs of high molecular weight (35%) [8], same type of assessment was carried out to investigate the concentration of PAHs in Chenab river in 2014 [9] and Indus river also in 2017 [10]. Polyaromatic hydrocarbons have adverse affects on human health and marine life, the permissible limit of PAHs in drinking water in Pakistan is 0.01mg/l [11]-[12].

When they exceeds the permissible limit in environment they have serious hazards to human health which include Gastrointestinal effect; Nausea, vomiting, abdominal pain, diarrhea, Respiratory effect; congestion, acute respiratory distress syndrome, Neurological effects; confusion, lethargy, vertigo fasciculation, convulsion, anesthesia cerebral oedema, coma, Hepatic effects; jaundice, hepatomegaly, elevated liver enzymes level, Ocular effect; ocular nerve atrophy, bilateral cataracts with chronic exposure [13], hemolytic anemia; in which red blood cells of body are damaged or destroyed and new red blood cells have not replaced them yet. Infants or newly born babies are vulnerable to this case because their immune system is not strong [14], PAHs once entered in a pregnant woman`s body they can be transferred into the child`s body [15] these conntaminats can enter our body via food also, vegetables grown on domestic or industrial wastewater, fruit, fish, animals meat [16]. Various materials and technologies have been used to remove PAHs from water including precipitation, ozonation,

oxidation, filtration, coagulation, ion exchange, reverse osmosis, activated carbons, titanium dioxide, alum sludge, agricultural waste, and synthetic resins[17], though these techniques and materials have some inadequacy in their processing to remove the pollutant from water as compared to advanced technologies and latest materials, nowadays adsorption process is widely used to treat contaminated water. This study is focused to evaluate the efficiency of graphene oxide to remove naphthalene and anthracene from surface water by adsorption process. The main objectives of the research are

1. To synthesize and characterize the graphene oxide
2. To evaluate the removal of naphthalene and anthracene from surface water of Hyderabd using graphene oxide

II. MATERIALS & METHODS

A. Materials

Fine Graphite particles, Potassium Permanganate (KMnO4), Sodium Nitrate (NaNO3), Suphuric Acid (H2SO4), Hydrogen per Oxide (H2O2), Distilled water, Hydrochloric Acid (HCL), Sodium hydroxide (NaOH), Naphthalene (C10H8) and Anthracene (C14H10) in solid form were bought from Sigma Aldrich (USA) and used during the experimental work.

B. Preparation of Graphene Oxide(GO)particles

When Graphene oxide was manually prepared through Hummer`s method by taking 2 gram of graphite particles, 2 gram of NaNO3 and 92 ml of H2SO4, mixed together in flask in ice bath for 4 hours, keeping the temperature of the mixture below 20`C, then 12 gram of KMnO4 were added to the mixture very carefully maintaining the temperature <20`C and stirred for 2 hours. Mixture was taken out from the ice bath and stirred for 1 hour at room temperature, and then 184 ml of distilled water was added to the mixture and stirred for 2 hours at the temp: of 90-95`C, keep in mind that mixture is not allowed to boil. After mixing for 2 hours at high temperature turned off the heater, added 100 ml of distilled water and kept on stirrer for 2 hours at room temperature. Added 40 ml of H2O2 solution with 30% of H202 and stirred for 1.5 hours, Graphene oxide is prepared. The pH value of prepared graphene oxide ranges between 1-2 so to make it neutral we washed it with deionized water at 4000-6000 rpm in centrifuge for 4 days and then filtere it with using wattman filters. The filtered graphene oxide was then kept in oven at 90`C for 40 minutes to evaporate the moisture from the GO particles.

C. Batch Adsorption Studies

Multiple concentration solutions of naphthalene & anthracene (1ppm, 5ppm, 10ppm, 15ppm, 20ppm) were prepared in round bottom flask of 50 ml of working volume, with weighed amount of 300mg of adsorbent (graphene oxide) and mixed by orbital shaker at 110 rpm for 90-120 minutes. pH of the solutions was adjusted by using HCL and NaOH. Affect of different parameters on adsorption process like; adsorbate concentration, reaction time, adsorbent dosage and pH value was investigated. Samples were analyzed on UV-spectrophotometer.

D. Adsorption Capacity Calculation

The adsorption capacity of the adsorbent was calculated by using the following equation;

$$q_e = \frac{(C_o - C_e)}{m} \times V$$

Where:

qe=Removal Capacity (mg/g),
Co= Initial concentration (mg/l),
Ce=Final concentration (mg/l),
V= Volume of the solution (l),s
m= Mass of graphene oxide particles (g).

III. RESULTS AND DISCUSSION

A. Characterization of Graphene Oxide (GO)

Figure 1 (a) represents the SEM image of synthesized graphene oxide at the magnification of 5µm in which it can clearly be seen that graphene particles have irregular shape and they are not of uniform structure, they have edges or pointy shape at the corners which helps the adsorption process to remove contaminants from water. In figure 1 (b) the result of dynamic light scattering technique (DLS) of graphene oxide particles is shown which indicates the average size of the graphene particles, graph shows the average size of GO particles was noted as 919 nm, measured by particle size analyzer (Malvern Instruments Ltd).

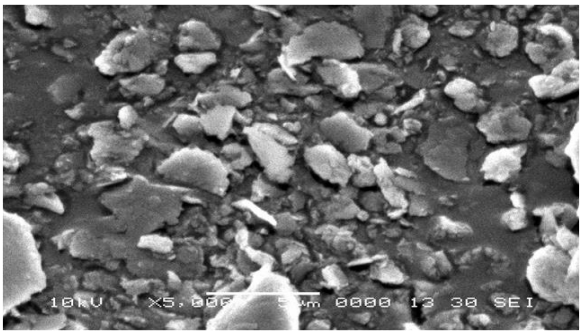
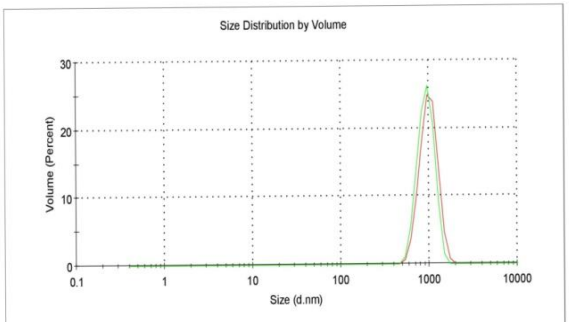


Figure 1 (a) SEM image of GO



(b) Dynamic Light Scattering (DLS) image

B. Adsorption Isotherms

The isotherms models Freundlich and Langmuir were used to check the experimental adsorption equilibrium data of naphthalene and anthracene on graphene oxide. These are the formulae of both isotherm models

$$q_e = K_f C^{1/n}$$ ***(Freundlich Isotherm)***

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b}\cdot\frac{1}{C_e}$$ ***(Langmuir Isotherm)***

Where ***qe****(mg/g)* represents the amount of adsorbate removed per unit mass of adsorbent, ***Ce****(mg/g)* is the adsorbate concentration remained after treatment. $\mathbf{K_f}$ and **1/n** are the Freundlich constants represent the adsorption capacity and adsorption intensity respectively. Langmuir isotherm constants are ***qm*** and ***b*** which are related to adsorption capacity of the adsorbent and rate of adsorption respectively. The Langmuir and Freundlich isotherms for naphthalene and anthracene adsorption are shown in figure 2 (a & b) and 3 (a & b) respectively. In this study both isotherms Langmuir and freundlich fit for adsorption of naphphalene whereas for the adsorption of anthracene Freundlich isotherm model fits more as compared to Langmuir isotherm.

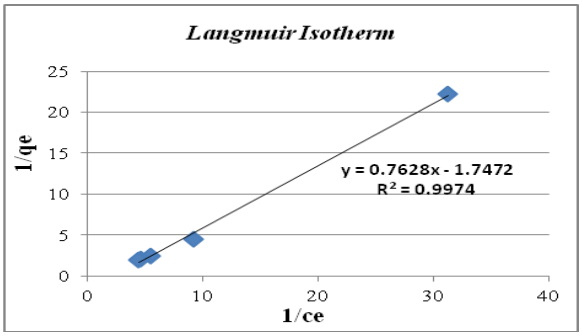
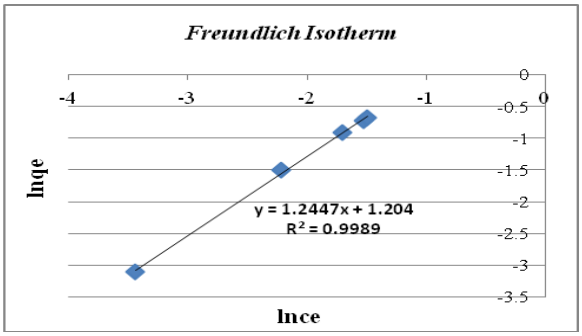


Figure 2(a): Langmuir Isotherm for naphthalene



(b): Freundlich Isotherm for naphthalene

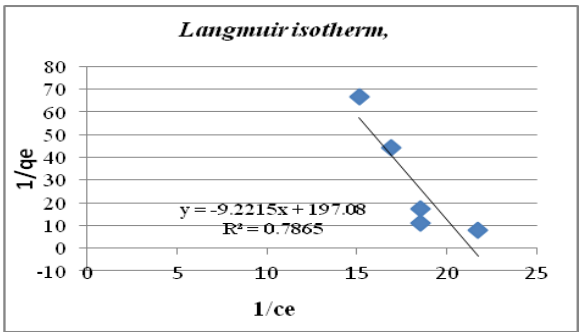
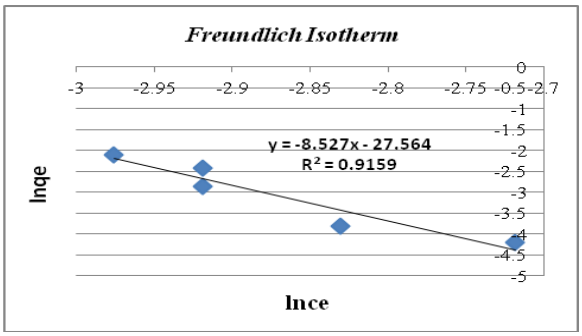


Figure 3(a): Langmuir Isotherm for Anthracene



(b) Freundlich Isotherm for anthracene

Langmuir and Freundlich isotherms show the linear relationship and values of R^2 for naphthalene adsorption are (0.99 & 0.99) it means both isotherms satisfy the adsorption process, and for anthracene adsorption the values of R^2 of Langmuir and Freundlich isotherms are (0.0.78 & 0.91) respectively, it shows that in this case Freundlich isotherm satisfies the adsorption process more than than Langmuir isotherm, because when the value of R^2 is closer to 1 the isotherm is considered to be best fit for the adsorption process.

C. Naphthalene and Anthracene Removal by Graphene Oxide

a) Effect of pH

The pH of the solution is considered as the basic and important parameter in the process of adsorption. In this research the effect of pH value for removal of anthracene and naphthalene from water by using graphene oxide was tested, pH value of naphthalene samples was adjusted as 2, 4, 6, 8, 10 and anthracene samples were made at different pH values as 2, 3, 5, 7, 9 with 20 ppm concentration, 300 mg dosage of graphene oxide was applied, contact time for naphthalene was 120 minutes and for anthracene it was 90 minutes. Results showed that 89% of naphthalene was removed at pH 2 because at higher pH value of sample the surface area of graphene oxide particles attain negative charge and gain weak interaction with naphthalene molecules [18]. The optimum removal 92.2% of anthracene was noted on pH 5; as the pH value of the sample increases from 5 the lesser removal of anthracene was observed, this might be attributed to the deprotonation of the requisite sites of the graphene. At lower pH value of sample the positively charged ions on the surface of GO becomes greater and proper adsorption occurs with negatively charged anthracene molecules. Same trend was observed in various studies [19]-[20]

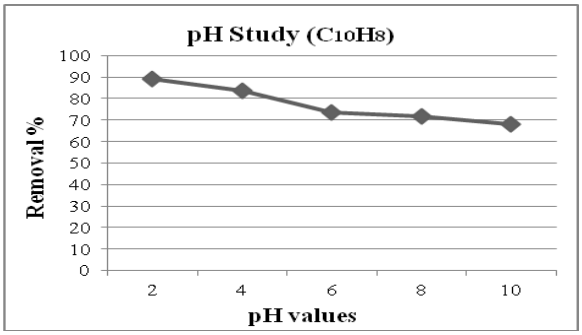
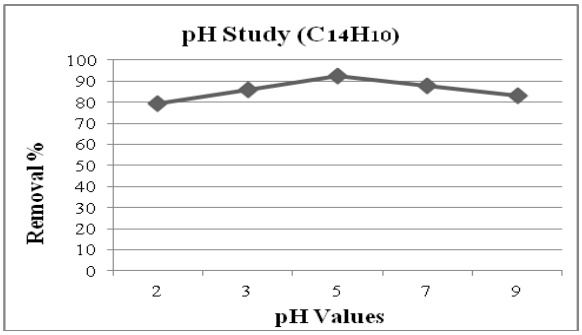


Figure 4 (a): Effect of pH on naphthalene removal



(b) Effect of pH on anthracene removal

b) Effect of initial concentration of Naphthalene & Anthracene

Effect of contaminants concentration was investigated by making multiple samples of different concentrations of naphthalene and anthracene as 1ppm, 5ppm 10ppm, 15ppm, and 20ppm, other parameters were kept the same as 300mg of GO dosage, reaction time for naphthalene was 120 minutes and for naphthalene it was set as 90 minutes on orbital shaker at 110 rpm, whereas the pH value of naphthalene samples was adjusted at 2 and anthracene samples were tested at pH 5 to evaluate the removal efficiency of GO by using the UV-spectrophotometer for analysis of samples. The results obtained from concentration study expressed that the maximum removal of naphthalene (93.16%) and anthracene (94.14%) was noted at 20 ppm, at lower concentration efficiency was less because there were limited available adsorption sites for such amount of adsorbent dosage. At 10 ppm concentration of naphthalene sample the adsorption equilibrium was achieved there was slight increase in removal efficiency after 10 ppm, whereas for anthracene huge variation in results were noted at different amounts of concentration, this can be attributed to overlapping of available functional groups on graphene oxide particle`s surface for lesser anthracene molecules to be adsorbed.

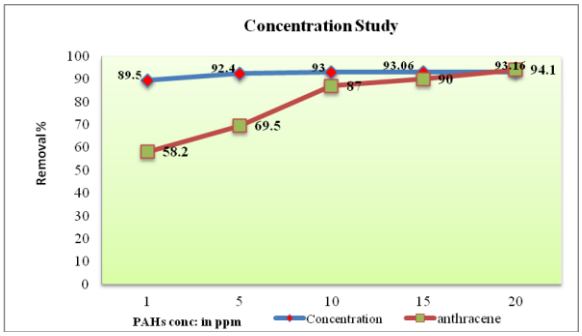


Figure 5: Effect of initial concentration on naphthalene & anthracene adsorption

IV. CONCLUSIONS

The results obtained through current experimental work revealed that GO particles posses great potential to remove naphthalene and anthracene from the water. The optimized conditions for maximum removal of naphthalene were observed at the pH value of 2, keeping the initial concentration of naphthalene as 20ppm in synthetically made sample, 93.16% of naphthalene was removed from the sample by using 300mg dosage of graphene oxide particles while the reaction time was noted as 120 minutes for maximum removal. For anthracene the optimum removal was recorded at the pH value of 5, in 20 ppm concentration of anthracene in sample, using 300mg of GO particles while the contact time was 90 minutes, 94.14% of anthracene was removed. All samples were analyzed on UV-spectrophotometer. The equilibrium data was tested on Langmiur and freundlich isotherms models. Both isotherms were fit for naphthalene adsorption and the values of $\boldsymbol{R^2}$ were (0.99 & 0.99), whereas for anthracene

adsorption Freundlich isotherm was best fit. The values of R^2 of Langmuir and Freundlich isotherms for anthracene were (0.78 & 0.91) respectively.

V. RECOMMENDATIONS

In current study graphene oxide is used to remove two compounds of Polyaromatic hydrocarbons (PAHs) family from water, it can be used to remove all PAHs from water. In this research batch study was performed to analyze the removal efficiency of graphene oxide for naphthalene and anthracene, in future column study can be done to adsorb naphthalene & anthracene from water by using GO as adsorbent. Graphene oxide can be synthesized from agricultural waste like wheat and rice straw, banana peel and other crops to utilize it for water treatment it would be huge progress to build an environment based on sustainable development. Heavey metals can also be removed from surface water as well as from drinking water by using graphene oxide. This material is cheap, easy to prepare and has outstanding efficiency to remove organic pollutants from water so it should be prepared commercially by the government to treat bulk amount of wastewater which is polluting our environment, rivers lakes and canals. Comparison of graphene oxide efficiency with other adsorbents can be done. It can be chemically modified in order to introduce more functional groups on the surface of GO particles to remove various contaminants. Reusability of graphene oxide particles can also be tested to remove the same or other pollutants from water.

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