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REMOVAL OF ANTHRACENE FROM SOLUTION USING [Cu(INA)$_2$] METAL-ORGANIC FRAMEWORKS SYNTHESIZED BY A SOLVENT FREE METHOD

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ABSTRACT
Metal-Organic Frameworks (MOFs) [Cu(INA)$_2$] were prepared by a solvent free method and were used for the adsorption of anthracene from solution. The [Cu(INA)$_2$] MOFs were found to be good adsorption materials having good adsorption capacity. The maximum adsorption capacity for the [Cu(INA)$_2$] MOFs was observed to be 22.73 mg/g for anthracene. The adsorption process favoured the pseudo-second-order kinetics and the Langmuir isotherm was found to be most appropriate model for the adsorption data. [Cu(INA)$_2$] MOFs, therefore, can be used as environmentally friendly adsorbents in the treatment of wastewater.

Keywords: *[Cu(INA)$_2$] MOFs (Copper – isonicotinic acid Metal-Organic Frameworks), Anthracene, Adsorption, solvent-free method.*

1.0 Introduction

Metal-Organic Frameworks (MOFs) designed by connecting metal ions to organic linkers forming a 3D porous framework and possessing diverse properties such as high surface area, uniform tunable pore size, functionalisable pore wall and flexible structure (Patil *et al.,* 2011). These properties make MOFs to be considered as potential candidates for application in catalysis, gas storage, drug loading and delivery, and adsorbents (Chowdhury *et al.,* 2009). In order to obtain the desired pore size, there is need for a rational and pragmatic approach to the selection of organic linkers and metals of suitable coordination which make MOFs versatile materials. Several Metal-Organic Frameworks have been synthesized mainly to exploit their adsorption properties, among these include MIL-100 (Peng *et al.,* 2015), MIL-53 (Patil *et al.,* 2011), (MIL = Material Institute Lavoisier), which proved to be very efficient sorption materials. The MIL-53 (Al) is of great interest because it is thermally stable up to 500 °C, which is an advantage over other MOFs (Patil *et al.,* 2011).

Availability of clean water is imperative for economic development and the steady increase in global population makes provision of clean water very important. However, contamination with various pollutants such as organic chemicals, has led to a decrease in availability of clean water resource (Hasan and Jhung, 2015). A lot of organic pollutants have been identified in natural water bodies which constitutes great threat to human and aquatic lives (Rasheed, 2013). The most common organic chemicals that are pollutants in water include dyes (Rasheed, 2013; Gupta and Suhas, 2009; Bao and Fang, 2012; Zhang *et al.,* 2011; Michael *et al.,* 2013; Bu *et al.,* 2013; Finizio *et al.,* 2011; Gong *et al.,* 2014; Johnson *et al.,* 1973)) persistent organic pollutants (POPs) which are carbon-based chemical compounds, and mixtures that include industrial chemicals such as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), and some organochlorine pesticides (OCPs), such as hexachlorobenzene (HCB) or dichloro-diphenyl-trichloroethane (DDT), dibenzo-p-dioxins (dioxins) and dibenzo-p-furans (furans) (Fawell and Ong, 2012). Polycyclic aromatic hydrocarbons, (PAHs), have also been known to be ubiquitous chemical contaminants which find their way into the environment by various human activities such as burning of fossil fuels, and incomplete combustion of wood and coal (Daughton, 2004; Daughton, 2005). Some adverse effects on human health such as carcinogenicity, immune-toxicity, and genotoxicity may result from the presence of PAHs in water (Pulkrabova *et al.,* 2008). PAHs are considered as priority pollutants because they are persistent even in low concentration and are also harmful to living organisms. Pollutions due to PAHs have been of high global concern due to their ubiquitous nature.

The first use of MOFs as adsorbent for the removal of dye was reported in 2010 using MIL-101-Cr and MIL-53-Cr (Cr = chromium), for the adsorptive removal of methyl orange (Perrin, 2012). They noted that the MOFs performed better than commercially activated carbon. A Cu-BTC MOFs (Cu = copper, BTC = 1,3,5-benzenetricarboxylic acid) was studied in the adsorptive removal of methylene blue and it was observed that pH plays an important role in the adsorption of methylene blue on the surface of Cu-BTC MOFs (Peng *et al.,* 2015; Haque *et al.,* 2010). A study of the adsorption mechanism of $[Cu(Imid)(H_2O)]^+$ (Imid = Imidazole), with flourescein, nile blue, nile red, and methyl red was carried out and it was observed that $[Cu(Imid)(H_2O)]^+$ readily adsorbs nile blue but cannot adsorb nile red (Lin *et al.,* 2014). The selective adsorption is due to the anionic part of nile blue which undergoes electrostatic interaction with the cationic MOFs $[Cu(Imid)(H_2O)]^+$. No interaction occurred between the non-ionic nile red and the MOF (Lin *et al.,* 2014; Nickerl *et al.,* 2013).

Electrostatic interactions were reported for the adsorption of PPCPs over MOFs in some studies (Nickerl *et al.,* 2013; Hasan *et al.,* 2012). Negatively charged naproxen anion was adsorbed on the positively charged MIL-101-Cr MOFs. Jung *et al.,* 2014, observed

the adsorption of 2,4-dichlorophenoxyacetic acid (2,4-D a highly toxic herbicide) onto MIL-53-Cr MOFs and activated carbon, and reported that the MOF showed a higher adsorption capacity for the herbicide, when compared with conventional activated carbon. It was observed that 2,4-D has p*K*a value of 2.7–2.8, and the isoelectric point of MIL-53-Cr was observed at pH 5. Favorable adsorption of 2,4-D was observed at pH 3-5. Lui *et al.,* 2014, also studied the adsorption of phenol and p-nitrophenol (PNP) from aqueous solutions on MOFs MIL-100-Fe, Cr and NH_2-MIL-101-Al, and compared with activated carbon. NH_2-MIL-101-Al was found to show exceptionally higher adsorption of PNP than the other MOFs studied and exceptionally higher adsorption selectivity for PNP than activated carbon. The excellent adsorption affinity was attributed to hydrogen bonding between PNP and the amino group in NH_2-MIL-101-Al MOFs.

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds with two or more fused aromatic rings. They have a relatively low solubility in water, but are highly lipophilic. Most of the PAHs with low vapour pressure in the air are adsorbed on particles. When dissolved in water or adsorbed on particulate matter, PAHs can undergo photodecomposition when exposed to ultraviolet light from solar radiation. In the atmosphere, PAHs can react with pollutants such as ozone, nitrogen oxides and sulfur dioxide, yielding diones, nitro- and dinitro- PAHs, and sulfonic acids. PAHs are formed mainly as a result of pyrolytic processes, especially the incomplete combustion of organic materials during industrial and other human activities, such as processing of coal and crude oil, combustion of natural gas and refuse, vehicular traffic, cooking and tobacco smoking, as well as in natural processes such as carbonization (Can, 2005; Liu *et al.,* 2014). Anthracene is an example of polycyclic aromatic hydrocarbons. It is insoluble in water and a component of coal tar. Anthracene is used in the production of the red dye, alizarin. Just like many other PAHs, anthracene is generated during combustion processes and exposure to humans happens mainly through tobacco smoke and ingestion of food contaminated with combustion products (Can, 2005; Anon., 2000). Apart from its toxicity problem, anthracene was chosen in this study because of its hydrophobic nature, having dimensions smaller or comparable to that of the MOFs channel, with increase in length and width, making it a suitable guest molecule to investigate the surface interactions.

Removal of anthrance from different media using diverse adsorbent materials has been reported. Owabor and Aluyor, 2008, reported the use of activated carbon prepared from groundnut shells for the bioremediation of anthracene contaminated soil. It was observed that adsorption proceeded quickly with an increase in temperature up to 900 °C. Abbasi *et al.,* 2013, studied the removal of anthracene from aqueous solution using silver nanoparticles prepared from plant extracts and observed that there was optimal removal of anthracene from the solution up to about 85%, which may be attributed to more functional groups present in the plant extract participating in binding of anthracene to the surface. However, no work has reported the removal of anthracene from aqueous solution using [Cu(INA)$_2$] MOFs synthesized by a solvent free method.

Therefore, we report the removal of anthracene from aqueous solution, by adsorption on [Cu(INA)$_2$] MOFs prepared by a green route approach (solvent free method). The effect of different parameters such as contact time, pH, temperature, initial concentration and adsorbent dosage on the batch adsorption process was also studied, while the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms equations were used to test their validity for the experimental equilibrium sorption data. Finally, desorption of anthracene from [Cu(INA)$_2$] MOFs was studied to determine the reusability of the MOFs.

2.0 METHODOLOGY

2.1 Materials and methods

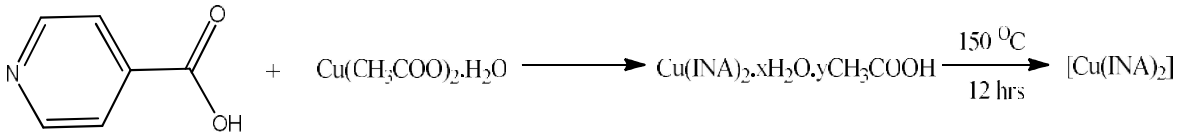
Isonicotinic acid (98%), copper acetate monohydrate ($Cu(CH_3COO)_2.H_2O$) (98.5%), and anthracene (95%) were purchased from Sigma Aldrich, United Kingdom, and were used as purchased. Stock solution of anthracene was prepared by dissolving anthracene in methanol and the range of concentration studied was obtained by successive dilution of the prepared stock solution.

2.2 Synthesis of [Cu(INA)$_2$] MOFs

[Cu(INA)$_2$] MOFs was synthesized by a solvent-free method as reported by Tella *et al,* 2014, 0.2 g of copper acetate monohydrate ($Cu(CH_3COO)_2.H_2O$) and 0.244 g isonicotinic acid were ground separately for 5 minutes and then mixed together and the mixture was shaken periodically for 30 minutes. The product obtained was heated at 150 °C for 12 hours to remove the glacial acetic acid trapped inside the pores of the [Cu(INA)$_2$] MOFs, and kept in a dessicator to cool after which it was stored in a sample bottle and used directly without further treatment in subsequent experiments.

2.3 Characterisation of the adsorbent

Elemental (CHN) analysis was carried out using a Perkin Elmer 204C microanalyser (Medac Ltd., Surrey, UK) and X-ray diffraction analysis was carried out using a Nonous Kappa CCD difractometer in the 2θ range of 4 – 40° using Cu Kα (λ = 1.5406Å). The Fourier transform infrared (FTIR) spectra of [Cu(INA)$_2$] MOFs before and after adsorption of anthracene was obtained on a Shimadzu 8400s spectrum FT-IR instrument (LAUTECH, Ogbomosho, Nigeria). The samples were mixed with KBr in the ratio 1:10 and pelletized, and the spectra were recorded over a wavelength range of 500 – 4000 cm^{-1}.



Batch adsorption studies

The batch adsorption studies were carried out by placing the adsorbent material, [Cu(INA)$_2$] MOFs (20 mg), in a 250 ml conical flasks and 25 ml of 1 – 25 mg/L solution of anthracene dissolved in methanol was added. The study was carried out by stirring at the rate of 168 rpm for 10 – 60 minutes and pH was adjusted to between 2 and 12 using 0.1 M HCl or NaOH. At equilibrium, the suspension was filtered and the filtrate immediately analyzed using Shimada UV Spectrophotometer UV–1800, at λ_{max}=344 nm. The amount of anthracene adsorbed on the [Cu(INA)$_2$] MOFs was calculated by subtracting the equilibrium concentration from the initial anthracene concentration.

$$q_{eq} = \left(\frac{C_o - C_{eq}}{m}\right).v \qquad (1)$$

where v is the volume of the solution in litres (L), m is the amount of adsorbent in grams (g); C_o and C_{eq} are the initial and equilibrium concentrations of anthracene (mg/L) .

A blank experiment was conducted to check the adsorption of anthracene on the walls of the flask, with the aim of authenticating and establishing the reliability and reproducibility of the results, and it was found to be negligible (Elaigwu *et al.,* 2014).

3.0 RESULTS AND DISCUSSIONS

3.1 Characterization of the adsorbent

The FTIR spectra of [Cu(INA)$_2$] MOFs synthesized, (Figure 1), shows the bands at 1602 cm^{-1} and 1417 cm^{-1} corresponding to asymmetric and symmetric stretching of the –COO group respectively.[1] The spectra of the [Cu(INA)$_2$] MOFs with adsorbed anthracene showed a shifting in the VC=C ring stretching from 1602 cm^{-1} of the MOF before adsorption to 1643 cm^{-1} after adsorption. The VC-H aromatic stretching of 3064 cm^{-1} observed in [Cu(INA)$_2$] MOFs before adsorption of anthracene was also shifted to 3084 cm^{-1} after adsorption.

The powder X-ray diffraction pattern of [Cu(INA)$_2$] MOFs, isonicotinic acid, and copper acetate are shown in Figure 2. The XRD pattern of the synthesized [Cu(INA)$_2$] MOFs using the solvent free method in this study confirmed that the synthesized material is [Cu(INA)$_2$] MOFs, and is in good agreement with the literature pattern of [Cu(INA)$_2$] MOFs synthesized through solvothermal method.

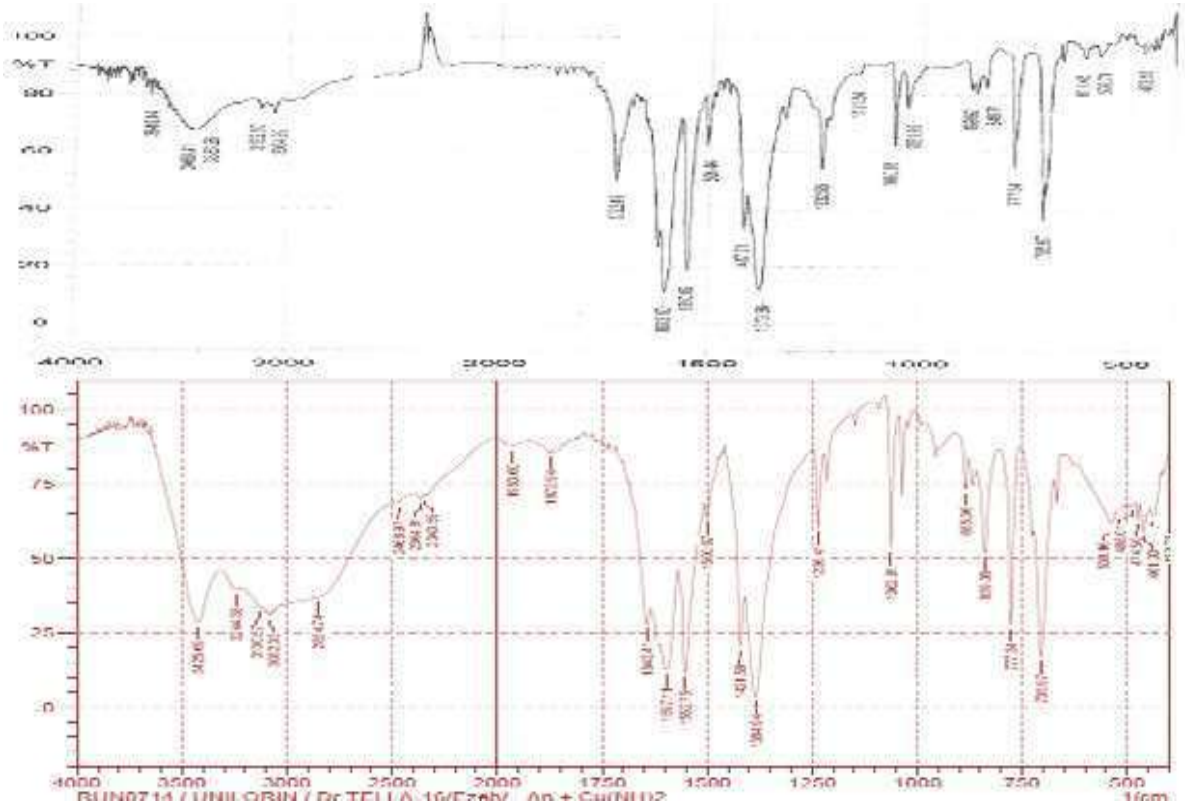


Figure 1: FTIR spectra of a) [Cu(INA)$_2$] MOFs b) [Cu(INA)$_2$] MOFs after adsorption of Anthracne

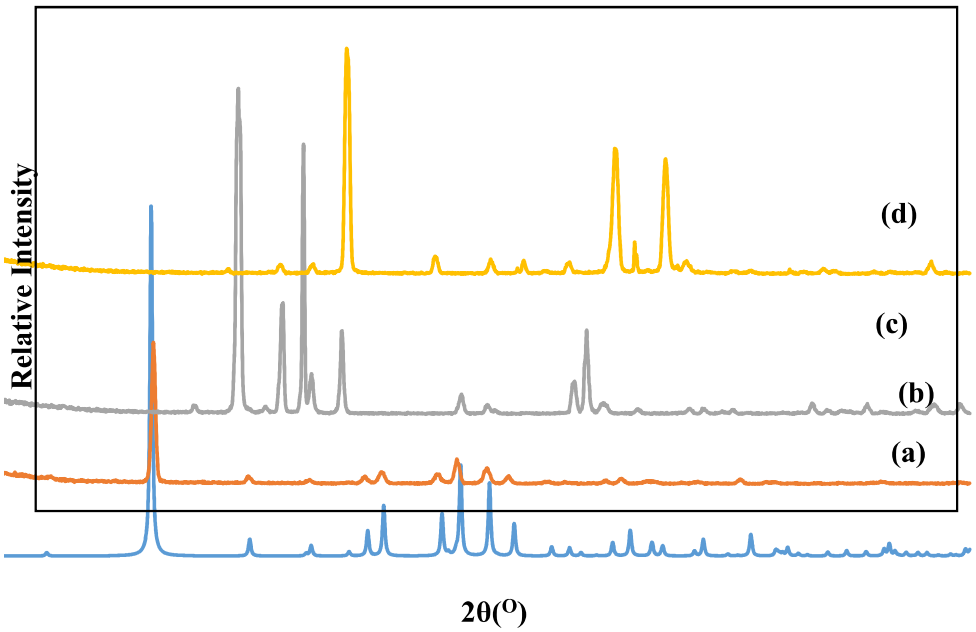


Figure 2: Comparison of XRD pattern of [Cu(INA)$_2$] MOFs and reactants (a) Simulated patterns of [Cu(INA)$_2$] from the single crystal data (b) Synthesized [Cu(INA)$_2$] (c) Copper acetate (d) Isonicotinic acid

3.2 Adsorption studies

3.2.1 Effect of pH

The experiment on effect of pH on the adsorption of anthracene from solution by [Cu(INA)$_2$] MOFs was performed at room temperature (32 ± 2 °C) using 20 mg/L adsorbate concentration and 20 mg of adsorbent for 30 minutes, and the result is shown in Figure 3. The study carried out over a pH range of 2-12 showed that the adsorption of anthracene on the [Cu(INA)$_2$] MOFs was unaffected with increasing pH as no significant change in the concentration of anthracene in the solution was observed on increasing the pH of the solution from 2-12 (Saad *et al.,* 2014; Rahmani *et al.,* 2010). The pH of the solution was adjusted either by using M HCl or NaOH solution.

3.2.2 Effect of adsorbent dosage

The result of the effect of adsorbent dosage on the adsorption of anthracene from solution is shown in Figure 4. The experiment was carried out at a temperature of 32 ± 2 °C using 2–30 mg adsorbent dosage, 20 mg/L adsorbate concentration for 30 minutes. It was observed that the amount of anthracene adsorbed from the solution increased as the dose of the adsorbent was increased from 2–20 mg before equilibrium was attained. The number of adsorption sites available for the adsorption is directly proportional to the quantity of adsorbent used in the experiment (Elaigwu *et al.,* 2014). Thus, increasing the quantity of adsorbent results in increase in the number of active sites available for the adsorption of anthracene from the solution, and hence, increase in the amount of anthracene adsorbed by the [Cu(INA)$_2$ MOFs (Eduardo *et al.,* 2004; Olgun and Atar, 2012; Salleh *et al.,* 2011; Umoren *et al.,* 2013; Stoltenberg *et al.,* 2012). However, the decrease in adsorption values noticed with further increase in adsorbent dosage from 20–30 mg suggests that most of the adsorbates have been adsorbed from the solution on the active sites of the adsorbent (Olgun and Atar, 2012).

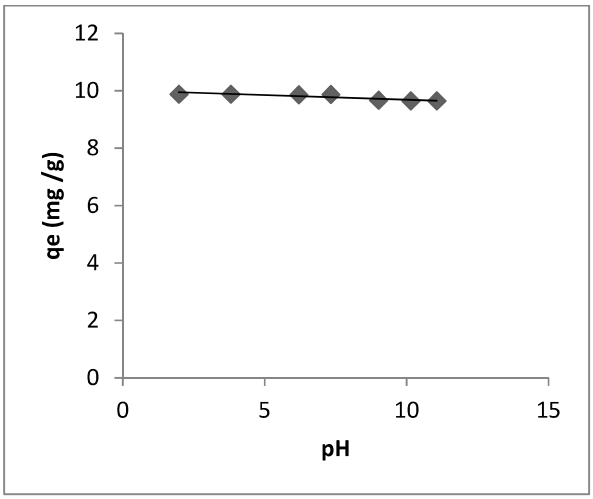


Figure 3: Effect of pH on the adsorption of anthracene over [Cu(INA)$_2$] MOFs. Concentration = 20 mg/L, temperature = 32 ±2 °C, speed = 168 rpm, time = 30 minutes

The result of the effect of temperature on adsorption of anthracene from solution by the [Cu(INA)$_2$ MOFs synthesized is shown in Figure 5. The experiment was carried out using 20 mg/L concentration of anthracene, 20 mg of [Cu(INA)$_2$] MOFs adsorbent at a pH of 4.99 for 30 minutes. There was a gradual decrease in the adsorption capacity over the temperature range of 30, 40, 50, and 60 °C. Increase in temperature was observed to decrease the anthracene adsorption process on the synthesized [Cu(INA)$_2$] MOFs. Thus, an increase in temperature weakens the interaction between the adsorbate and adsorbent molecules (Rasheed, 2013).

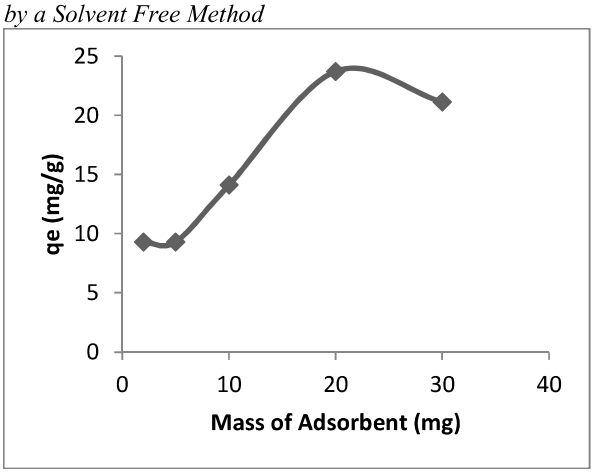


Figure 4: Effect of adsorbent dosage on the adsorption of anthracene over [Cu(INA)$_2$] MOFs, at temperature = 32 ± 2 °C, Concentration = 20 mg/L, pH = 4.99, speed = 168 rpm, time = 30 minutes

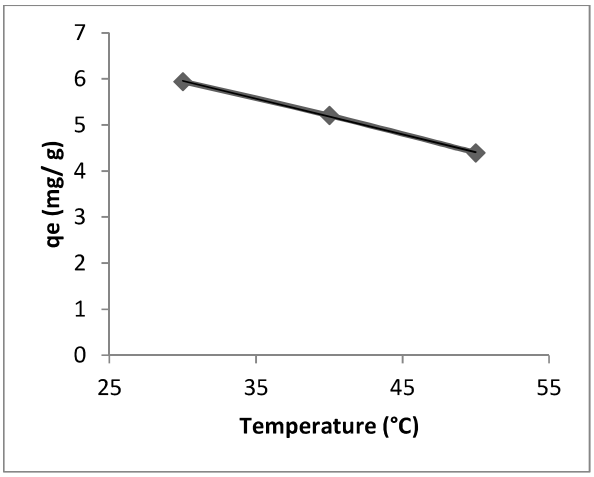


Figure 5: Effect of temperature on the adsorption of anthracene over [Cu(INA)$_2$] MOFs at Concentration = 20 mg/L, pH = 4.99, speed = 168 rpm, time = 30 minutes

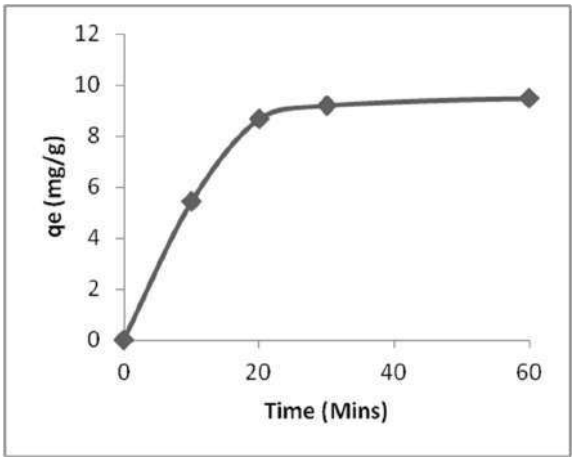


Figure 6: Effect of contact time on the adsorption of anthracene over [Cu(INA)$_2$] MOFs at 32 ± 2 °C, Concentration = 20 mg/L, pH = 4.99, speed = 168 rpm, time = 60 minutes

3.2.3 Effect of temperature on adsorption

3.2.4 Effect of time and adsorption kinetics

The effect of time on the adsorption of anthracene from solution by [Cu(INA)$_2$] MOFs is shown in Figure 6. The experiment was performed at a temperature of 32±2 °C using 20 mg/L solution of anthracene and 20 mg of [Cu(INA)$_2$] MOFs at a pH of 4.99. The contact time was varied between 10 and 60 minutes in order to establish the equilibrium time. The adsorption of anthracene rapidly increased for the first 20 minutes and then slowly increased up to 30 minutes and remained constant thereafter. Majority of the anthracene removal occurred in the first 30 minutes accounting for 9.20 mg/g on the [Cu(INA)$_2$] MOFs. The initial increase in adsorption observed is attributed to the availability of a number of vacant adsorption sites which became occupied with time and so adsorption occurred at a slow rate after about 30 minutes (Olgun and Atar, 2012; Chen *et al.,* 2011). Thus, 30 minutes was taken as the time required to attain equilibrium for the adsorption process in this study.

The adsorption kinetic studies were carried out using linear plots of the pseudo-first-order and pseudo-second-order kinetic models, (Figure 7).

The pseudo-first-order rate equation relates the adsorption rates to amount of anthracene adsorbed at time "t". It is expressed by:

$$\frac{1}{q_t} = \left(\frac{k_1}{q_{eq}}\right)\left(\frac{1}{t}\right) + \left(\frac{1}{q_{eq}}\right) \qquad (2)$$

The pseudo-second-order rate equation is expressed by

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}} t \qquad (3)$$

where q_{eq} and q_t are the amount of anthracene adsorbed per unit mass of the adsorbent (mg/g) at equilibrium and time, t, respectively; k_1 is a pseudo-first-order kinetic constant expressed in min^{-1} and k_2 (gmg^{-1}min^{-1}) is the pseudo-second-order rate constant.

The pseudo-first-order, and pseudo-second-order kinetics results for this study are shown in Table 1. The correlation coefficient (R^2) value for the pseudo-second-order was observed to be higher than that of the pseudo-first-order kinetics model; which indicates that the experimental data obtained in this study fitted into the pseudo-second-order kinetic model more than the pseudo-first-order kinetic model.

Table 1: Pseudo first- order and pseudo second order constants of anthracene

Kinetic Model	Rate constant	R^2
Pseudo- second order k_2 (g/ mg/ min)	8.81 x 10^{-3}	0.9994
Pseudo- first order k_1 (min^{-1})	4.5 x 10^{-3}	0.9118

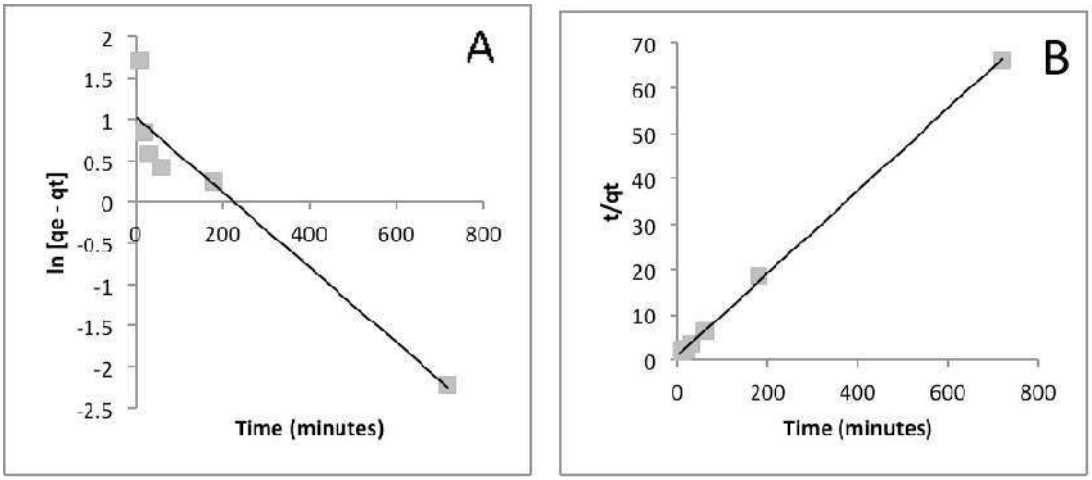


Figure 7: (A) Pseudo-first-order kinetic plot of Anthracene (B) Pseudo-second-order kinetic plot of athracene

3.2.5. Effect of initial concentration and adsorption isotherms

The effect of initial concentration of anthracene on adsorption experiment was performed at 30 ± 2 °C, for 30 minutes using 1-25 mg/L adsorbate concentration, 20 mg of adsorbent, [Cu(INA)$_2$] MOFs, at pH of 4.99, and 168 rpm. It was observed that adsorption increased with an increase in concentration up to 20 mg/L. The effect of the initial concentration depends on the immediate relation between the available binding sites on an adsorbent surface and the PAHs concentration (Elaigwu *et al.,* 2014; Umoren *et al.,* 2013). Thus, at low concentration of anthracene, there exist unoccupied adsorption sites on the [Cu(INA)$_2$] MOFs which became occupied with an increase in anthracene concentration. Hence, the adsorption process slowed down due to the reduction in the number of adsorption sites available for the anthracene molecules. This accounts for the decrease in the amount of the anthracene molecules adsorbed at concentrations beyond 20 mg/L (Chen *et al.,* 2011; Eren and Acar, 2006; Olgun and Atar, 2012).

The Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherm models were used to describe the adsorption characteristics of anthracene on the [Cu(INA)$_2$] MOFs. The linear forms of the models are:

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{K_L . q_{max}} + \frac{C_{eq}}{q_{max}} \text{ (Langmuir model) (4)}$$

$$\log q_{eq} = \log K_F + \frac{1}{n}\log C_{eq} \text{ (Freundlich model) (5)}$$

$$q_{eq} = B \ln A_T + B \ln C_{eq} \text{ (Temkin model) (6)}$$

$$\ln q_{eq} = \ln(q_s) - (K_{ad}E^2) \text{ (Dubinin} - \text{Radushkevich model) (7)}$$

where q_{max} is the maximum adsorption capacity (mg/g), q_{eq} is the amount of anthracene adsorbed per unit mass of the adsorbent at equilibrium (mg/g), C_{eq} is the equilibrium concentration of adsorbate (mg/L), n is the intensity of the adsorption constant, K_F (mg/g) is the adsorption capacity for Freundlich model, K_L (L/mg) is Langmuir constant relating to adsorption strength or intensity, A_T is Temkin isotherm equilibrium binding constant (L/g), B is the constant related to heat sorption (J/mol/K), q_s is the theoretical isotherm saturation capacity (mg/g), K_{ad} is the Dubinin-Raduskevich isotherm constant, E is the mean free energy (KJ/mol).

Figure 8 presents the result of the effect of initial concentration of anthracene on the adsorption process while Figure 9 shows the linear plots of Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherms.

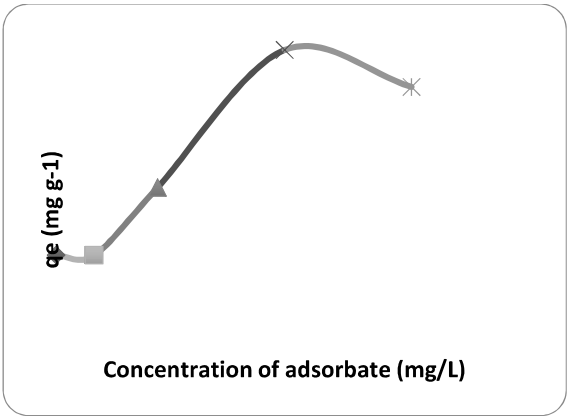


Figure 8: Effect of initial conc. on the adsorption of anthracene over [Cu(INA)$_2$] MOFs at 32 ± 2^{0}C, pH of 4.99, 168 rpm, time = 30 minutes

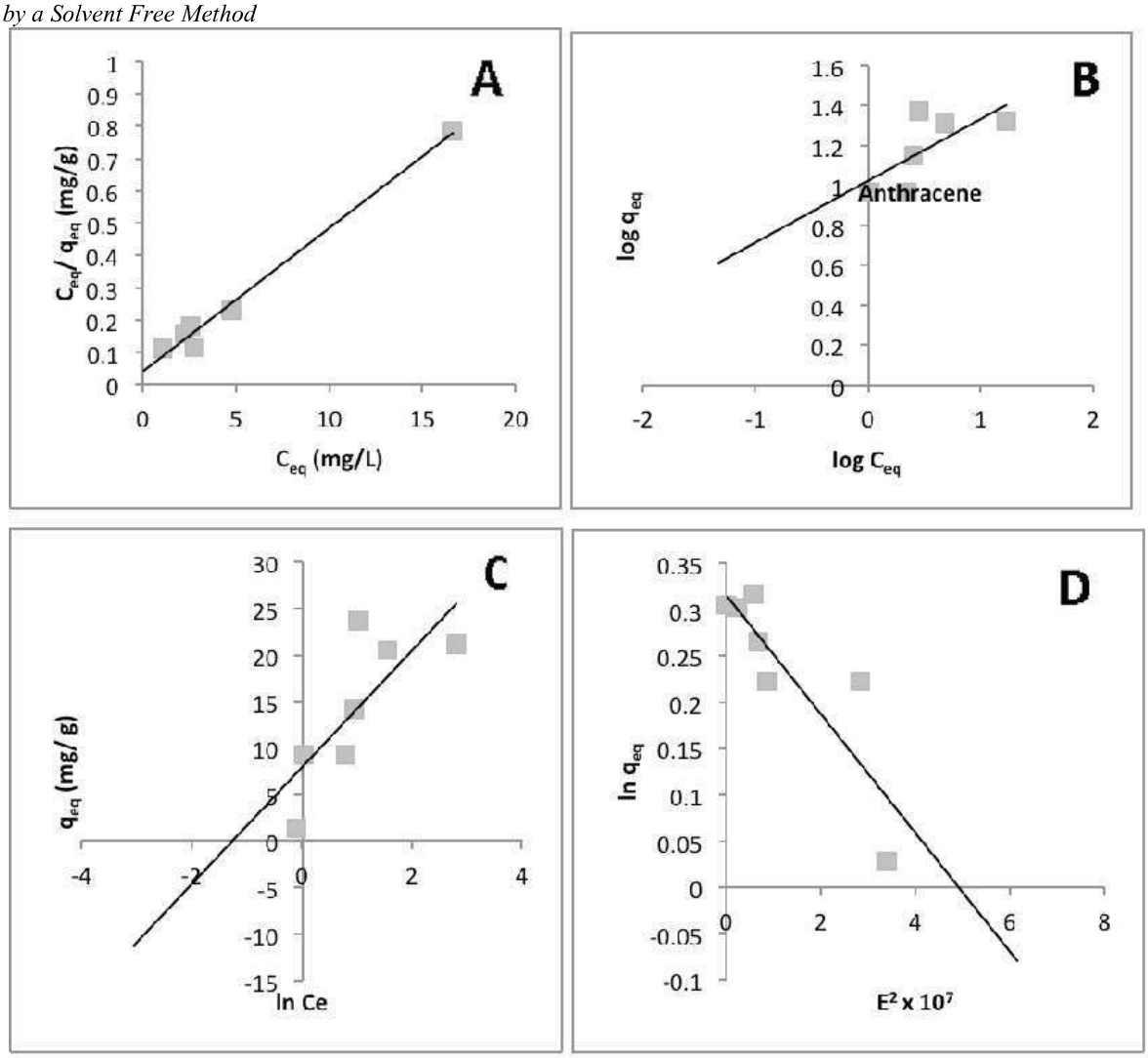


Figure 9: Adsorption Isotherms (A) Langmuir (B) Freundlich (C) Temkin (D) Dubinin

Table 2 gives a summary of the theoretical parameters for the isotherms used in this study and their corresponding R^2 values. The R^2 value for the adsorption of anthracene onto the [Cu(INA$_2$)] MOFs was found to be highest for the Langmuir model, implying that the adsorption data fitted best the Langmuir model. The maximum adsorption capacity from the Langmuir isotherm was found to be 22.73 mg/g.

Table 2: Adsorption Isotherms parameters for Anthracene

PAHs	Langmuir Constants			Freundlich Constants			Temkin Constants			D-R Constants		
	q_{eq} (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)	n	R^2	B (J/mol/K)	A_T (L/g)	R^2	q_s (mg/g)	E (kJ/mol)	R^2
Anthracene	22.73	1.0476	0.9873	10.52	3.225	0.4757	396.48	3.543	0.577	3.161	1.104	0.735

4.0 Conclusion

[Cu(INA$_2$)] MOFs, prepared by solvent free method, and tested successfully for the removal of anthracene from solution is presented in this study. The kinetics of the adsorption of anthracene onto the [Cu(INA$_2$)] MOFs followed a pseudo-second-order rate law with the Langmuir isotherm being the best model to describe the adsorption data. The kinetic study showed that equilibrium was reached within 30 minutes. There was no significant effect of pH on the adsorption process. Our results in this study shows that the [Cu(INA$_2$)] MOFs, synthesized under environmentally friendly condition, could be used as an effective adsorbent materials for the removal of anthracene from wastewater.

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