

ADSORPTIVE CAPACITY OF ALUMINA AND COBALT DOPED ALUMINA HYBRID FOR THE REMOVAL OF POLYAROMATIC HYDROCARBONS: KINETICS AND ISOTHERM STUDY

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Polyaromatic hydrocarbons are listed as priority pollutants due to high mobility and long persistence in the environment. It is basically the by-product of incomplete combustion of organic material (wood, coal, oil) having mutagenic and carcinogenic effect which is need to be address. The present study is an attempt to propose the model for the remedial of polyaromatic hydrocarbons using organic-inorganic hybrid materials. Time dependant batch experiments were used at fixed adsorbent dose (5mg) and adsorbate concentration (0.01mg/l) to study the adsorption of polyaromatic hydrocarbons. FTIR results showed O-H ($3504-3416\text{cm}^{-1}$), C-H ($2935-2985\text{cm}^{-1}$), Al-O ($1200-400\text{cm}^{-1}$) and hybrid formation (Al-O-C) band ($1111-1093\text{cm}^{-1}$). SEM micrograph showed amorphous nature of alumina hybrid supported by XRD result. TGA data showed the resistive behaviour with maximum residual upto 77%. The adsorption rate of alumina hybrid showed 68% naphthalene, 65% anthracene and 51% pyrene. Pseudo second order ($R=0.999$) and freundlich isotherm ($R=0.9989$) is best fitted to explain the multilayer adsorption capability.

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1. Introduction

Polyaromatic hydrocarbons (PAHs) are the by-products of incomplete combustion of organic materials containing one or two fused benzene rings [1, 2]. These are hydrophobic, volatile and non-biodegradable in nature having carcinogenic and mutagenic effects. Due to its persistent nature once they enter into the water systems; it is difficult to be removed. PAHs are listed as US-EPA and EU priority pollutants [3] and their concentrations need to be controlled. Paint, rubber, cement, petrochemical, and solvent manufacturing industries are the main source these kind of pollutants into water reservoir. Last few decades, different treatment techniques have been used [4] such as precipitation, oxidation, floatation, gravity separation, coagulation, distillation, solvent extraction, micro and ultra-filtration, electrolysis. It seems to be uneconomical due to multi-step processes, high capital and operational cost, additional requirement of chemical. Scientific community is in the quest of finding more economical method for the remedial of PAHs. However, adsorption technique emerged as an effective and economical method [5]. Different nature of adsorbents (organic and inorganic) were synthesized and applied on bench scale resulted different efficiencies. Pursuing different material, new class of material is formed with novel properties i.e., hybrid. Different hybrid materials such as Chitosan/CNTs [6], polydopamine coated iron oxide [7], Grafted cellulose [7], pine bark [8], EDTA-modified polystyrene [9] (Li et al, 2012), ferric oxide loaded glycidyl methacrylate [10]; amine modified polyglycidyl methacrylate grafted cellulose [11]), polyaniline/palygorskite composite [12], nano-silica modified nanopolyaniline [13], activated carbon [14], sulfonic acid functionalized SBA-15 [15], disulfonato-Silica [16], polymer grafted alumina [17] have been reported for the remediation of different

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pollutant. Alumina is the porous material having high surface area with thermal and mechanical stability. Due to its unique properties, it has employed as inorganic moiety for the synthesis of hybrid material. The present study is an attempt to synthesize the alumina hybrids as multifunctional material for the remedial of naphthalene, anthracene and pyrene.

2. Material and Method

2.1. Synthesis protocol of alumina hybrids

Hybrid materials are synthesized using aluminium nitrate nano-hydrate and D-glucose adopting the sol gel method [18, 19]. The schematic layout is presented in fig.1. It is understood that the mixture of aluminium nitrate nano-hydrate and D-glucose interact with each other through hydrogen bonding, thus affecting the surface morphology in polarized media resulted in hybrid formation.

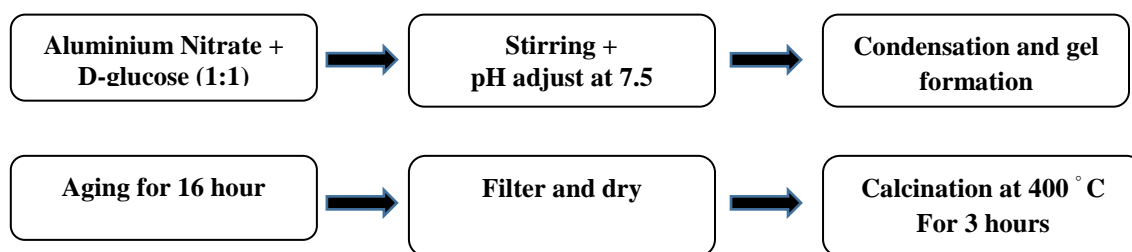


Fig. 1. Schematic synthesis layout of organic-inorganic hybrids

2.2. Characterization

As synthesized alumina hybrids were characterized by standardized techniques (FTIR, SEM-EDX, XRD and TGA) to study the structural, morphological, compositional, and thermal characteristics of the materials.

2.3. Batch Adsorption Experiment

Independent batch experiments were conducted to evaluate the adsorption behaviour of alumina hybrids towards polyaromatic hydrocarbons as a function of time. Known concentration (0.1 mg/l) of synthetic solution of naphthalene, anthracene and pyrene were pipette out into series of cultural vial containing 5 mg of each synthesized hybrid material (as adsorbent). At regular intervals of contact time (in minutes) between adsorbent and adsorbate, the solution was filtered. An aliquot was run on standardized analytical equipment to determine the amount of adsorbate adsorbed per unit mass of the adsorbent. The percentage removal was calculated using this equation:

$$\% \text{ Adsorption } (R_{\text{ads}}) = \frac{C_i(\text{PAH}) - C_f(\text{PAH})}{C_i(\text{PAH})} \times 100$$

R_{ads} = removal, C_i = initial concentration (mg/L) in solution used, C_f = final concentration (mg/L) in solution at equilibrium.

2.4. Adsorption Kinetics and Isotherms

The well-established adsorption kinetics (first order, pseudo-first order, pseudo-second order and intra-particle diffusion) and isotherms (Langmuir and Freundlich) were applied on experimental data to understand the adsorption mechanisms (adsorption rate and capacity) of synthesized alumina hybrids. The best-fitting was evaluated by linear regression (R^2) showed the

conformity between experimental data with predicted model values (close or equal to 1). High correlation coefficient value indicates that model successfully describes the kinetics of adsorption.

The linear equations are as under

$$1/q_e = 1/Q_o + 1/bQ_oC_e \quad (\text{Langmuir isotherm})$$

$$\log q_e = \log \left[K_f + (1/n) \log C_e \right] \quad (\text{Freundlich isotherm})$$

$$\log Ct = \frac{K_1}{2.303} t + \log C_o \quad (\text{First order})$$

$$\log(q_e - qt) = \log q_e - \frac{K_1 t}{2.303} \quad (\text{Pseudo first order})$$

$$t/qt = 1/K_2 q_e^2 + t/q_e \quad (\text{Pseudo second order})$$

$$\log R = \log K_{id} + \log(t) \quad (\text{Intra-particle diffusion})$$

3. Result and discussion

3.1. FTIR

Organic-inorganic hybrids exhibited main functional group O-H, C-H, Al-O-C (see Table 1). The broad absorption band of O-H (str) at 3504-3416 cm^{-1} showed presence of moisture content in the lattice of hybrid material. It is extensively reported by a number of researchers [20, 21]. The small and less intense band at 2935-2985 cm^{-1} assigned to the C-H stretching mode [21] indicate the presence of glucose. The absorption band observed at 2345-2364 cm^{-1} and 1261-1195- cm^{-1} are attributed to the stretching and bending vibrations of C-O due to adsorbed carbon dioxide from atmosphere. It is evident that synthesis (alumina hybrids) was undertaken at ambient temperature and pressure. The synthesis of hybrid (alumina: glucose) is verified by the sharp and intense bands at 1383-1386 cm^{-1} and 1111-1093 cm^{-1} assigned to hybridisation of alumina (Al-O) with aldehyde (O-CH) and carbonyl group (-C=O) of glucose, forming Al-O-CH as reported by [22]. Further probing of absorption band at 1022- 993 cm^{-1} indicates bending vibration of Al-(OH) as reported by Xue [23], whereas characteristic absorption bands of main aluminium oxide [24] appears in the region 1200-400 cm^{-1} . Coordination of alumina matrix (Al-O-Al) in AlO_4 at 669-619 cm^{-1} and in AlO_6 [25] reflects at 802-785 cm^{-1} .

Table 1. FTIR Frequencies of Alumina hybrid.

Frequencies (cm^{-1})	Assignment	Literature cited
3487 and 1647	H-O-H (str, b) due to absorbed moisture	Nasiri et al., 2011; Tabatabaee and Saberi 2013
2935	C-H (str) C_1	Saikia, & Parthasarathy, 2010
2359 and 1261	--CO due to adsorbed CO_2 (str,b)	Chen, et al., 2009
1383	Al-O—CH(str, sharp) indication of Hybrid formation	Khosla et al., 2013; Boumaza et al., 2009
1095	Al-O-C / (Al-O-Al)	Ibrahim et al., 2006; Boumaza et al., 2009
1020	Al-OH deformation linked to Al ion	Xue et al., 2007; Boumaza et al., 2009
669	Al-O-Al (AlO_6)	El-Amir et al. 2016

3.2. Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX)

Scanning electron microscopy (SEM) of organic-inorganic alumina hybrids showed irregular shaped blocks with small coarse particles dispersed on surface [26] as shown in fig. 2. The particle size is also assessed from micrograph ranges from 27nm-40nm showed narrow pore size distribution. Narrow distribution is also reported by for mesoporous polymer and homologous

carbon framework. Elemental composition of organic–inorganic hybrids is determined through energy dispersive x-ray spectrometer coupled with SEM (see fig 3). It is encouraging to note that a significant amount of aluminium and carbon confirmed the successful synthesis of hybrids material.

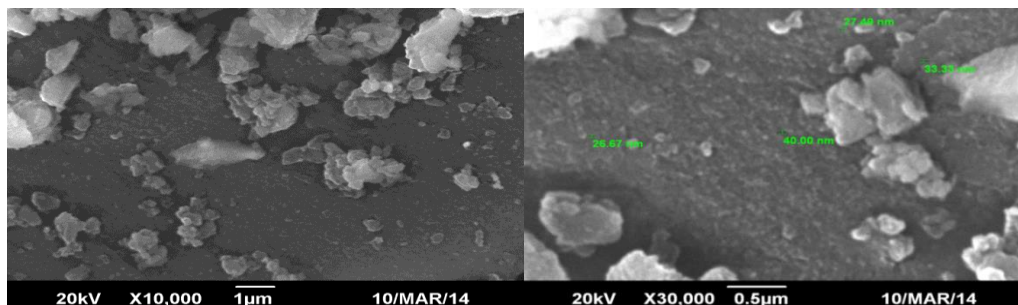


Fig. 2. SEM of alumina hybrids at different magnification power (10,000 X and 30,000X)

3.3. X-ray diffractometer (XRD)

The synthesized hybrid material are analyzed on X-ray Diffractometer (JEOL JDX-II) using Cu K α radiation ($\lambda = 0.15406$ nm). It showed that hybrid is of amorphous in nature (see Fig 4).

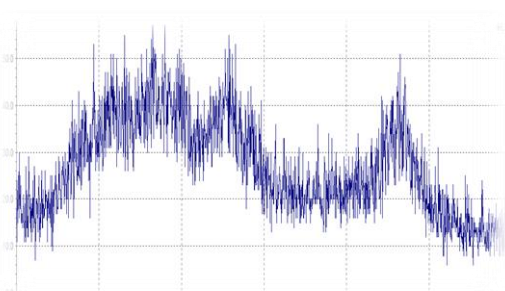


Fig. 3. EDX of alumina hybrid

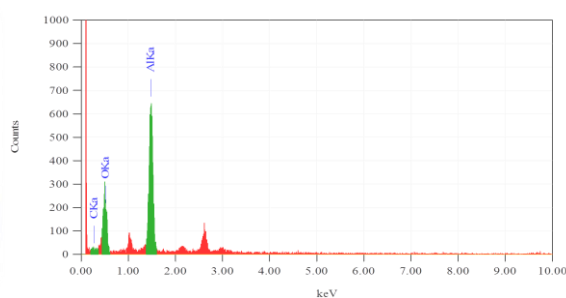


Fig. 4. XRD pattern of alumina hybrid

3.4. Thermo-Gravimetric Analysis (TGA)

Thermo-gravimetric analysis of synthesized alumina hybrids was performed on a TG (Perkin-Elmer Diamond Series) system at inert environment with a heating rate 20°C per min up to 600°C. It showed the relationship of mass loss with temperature. An increase in weight loss with increasing temperature is generally observed for the samples comprising of one or two decomposition steps. An initial decline in mass is more rapid about 17% at 35-182°C in the first step while 19% at 185-450°C second step of decomposition (see fig 5). It is also noted that significant amount of material remains as residue (77%). This might be due to complete decomposition of the material leaving behind carbon ash as residue. This is encouraging that materials are degraded at much lower temperature than the energy intensive treatments of decomposition.

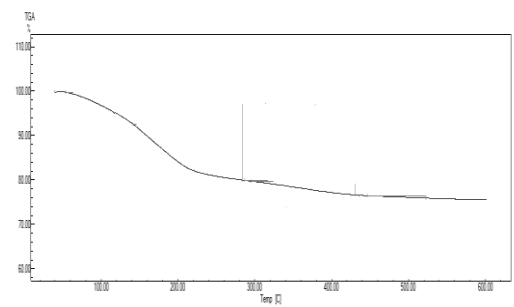


Fig. 5. TGA spectra of alumina hybrid

4. Batch experiment

Time dependent batch experiments were conducted to determine the removal efficiency of synthesized alumina hybrid towards polyaromatic hydrocarbons (naphthalene, anthracene and pyrene). Each batch experiment was conducted at known adsorbate concentration (0.1mg/L) and adsorbent dose (5 mg) as a function of time till equilibrium is attained. For each observation, minimum of 2-5 minutes was provided for adsorbate to adsorbent contact. The solution was filtered and run on standardized analytical instrument i.e., UV-Vis Spectrophotometer (UV-1601 Shimadzu, Japan) for the determination of residual polyaromatic hydrocarbons concentration. The absorbed concentration was determined from standard calibration curves.

4.1. Adsorption of Naphthalene

Naphthalene is simplest polyaromatic hydrocarbons consists of two fused benzene ring. It has good affinity towards organic compounds due to same nature. Alumina hybrids are subjected to adsorb the naphthalene, initially adsorption increase with increase in contact time. It is due to available vacant spaces on surface. Later on, it started to decrease when vacant spaces on surface got filled. The present study results are in consistent with same observation [27, 28]. It is interesting to note that contact of 12 minutes can be regarded as crossing point or the phase transition time for hybrids as shown in fig.6. Optimum removal of naphthalene is found to be 68%. Abu Ellela *et al.*, [29] is observed 50% naphthalene removal within 10 minutes.

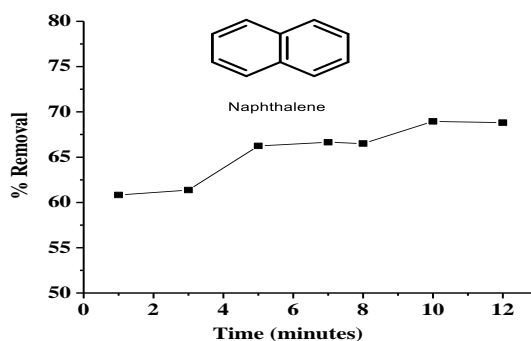


Fig. 6. % Removal of Naphthalene using synthesized hybrid as function of time

4.2. Adsorption of Anthracene

Anthracene consists of three fused benzene ring. It is the component of coal tar. It is generally noted that an initial rapid increase in adsorption become relatively slowed down with increasing in contact time. This delay is directly related to the saturation of available sites with

adsorbate, limiting the rate of adsorption. Same trend is also noted for the adsorption of anthracene using activated carbon [30]). Further probe showed that alumina hybrid is capable of removing anthracene upto 65% at 14 times as shown in fig.7. The mechanism proposes that negatively charged (hydrophilic) surface of hybrid attracts the positively charged (PAHs). This is further facilitated by the available surface active sites.

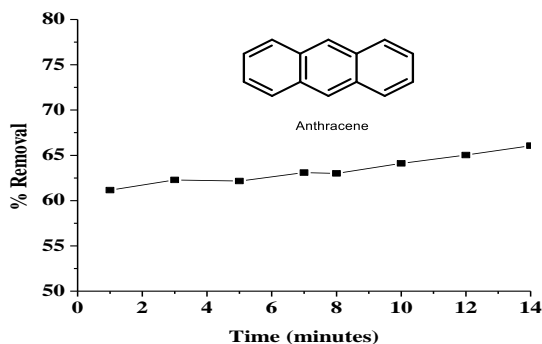


Fig. 7. % Removal of Anthracene using synthesized hybrid as function of time

4.3. Adsorption of Pyrene

Pyrene is four ringed poly-aromatic hydrocarbon, having angular arrangement. Pyrene is a π -electron donor able to bind with π -electron acceptor. Synthesized alumina hybrids showed the removal efficacy towards pyrene [31]). Although its removal efficiency with respect to other selected PAHs is less due to increase in molecular size. It showed maximum 51% removal of Pyrene within 12-14 minutes of contact (see fig 8).

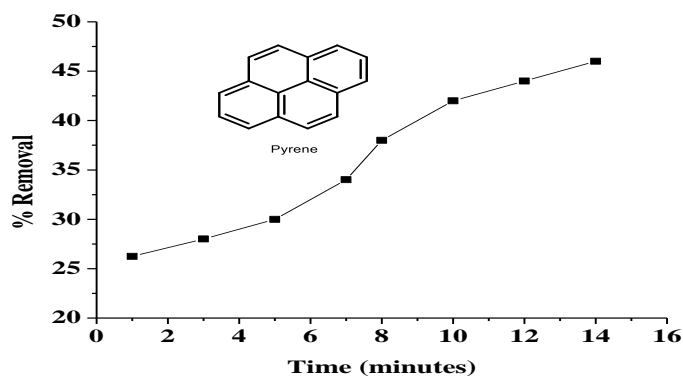


Fig. 8. % Removal of Pyrene using synthesized hybrid as function of time

4.4. Comparative Analysis

Comparative analysis of selected polycyclic aromatic hydrocarbons on the synthesized alumina hybrids concludes at the following sequence:



This trend is attributed to the molecular size, higher the molecular size, less is the adsorption. This further explains that the increase in adsorbate molecular size decreases in adsorption, due to steric hindrance provided by the relatively bulkier groups on adsorbent

surface[32]. Bulky/ larger molecules cannot access or diffuse into internal microspores, offering lower adsorption capacity. Similar trend is also observed for the removal of naphthalene, phenanthrene and pyrene using carbon nanomaterial [33].

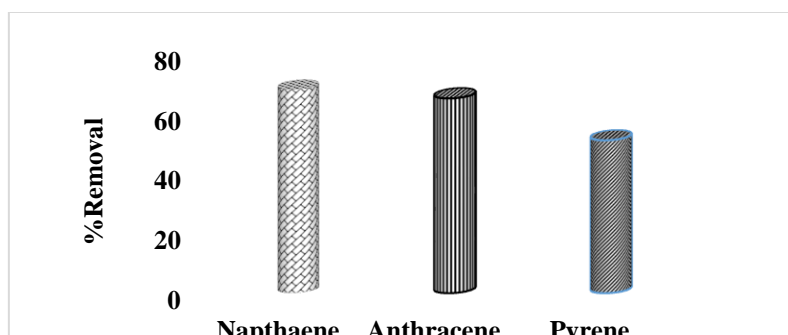


Fig. 9: Comparative analysis of different PAHs using alumina hybrids

4.5. Proposed Mechanism for Poly-aromatic hydrocarbons Removal

Surface polarity is the important property affecting the adsorption capacity. The synthesized alumina hybrids contained sufficient oxide and hydroxide groups contributing the negative charged on its surface (hydrophilic) prone to attract for electron positive charged (electron deficient species). The polarity difference between adsorbate and adsorbents are responsible for separating different compounds from bulk solution. In the case of poly-aromatic hydrocarbons, π - π interactions [34] are involved for adsorption due to hydrophobic nature of adsorbate. In the initial stage, PAHs adsorbed/diffused from bulk solution to external surface area of adsorbent rapidly. To reach the adsorption-desorption dynamic equilibrium, pore on surface provide the access for mass transfer from adsorbed external surface into the inside the adsorbent reached interior active sites, from where it can diffuse/bind with available active sites.

4.6. Adsorption of PAHs from Industrial waste

The combusted waste material containing organic material produces fly ash, flue gas and heat. Incinerator fly ash contained organic and inorganic constituents [35]. Fly ash sample was collected from the incineration plant from National Cleaner Production Centre (NCPC), Morgah Rawalpindi. Poly-aromatic hydrocarbons are extracted from fly ash using n-hexane (see figure 9). Selected PAHs (naphthalene, anthracene and pyrene) were studied at their respective λ max (222 nm, 252 nm and 273 nm) using alumina hybrids. Alumina hybrid were applied as adsorbent, showed maximum removal of naphthalene (59 %), anthracene (38%) and pyrene (28%). It is observed that % removal of PAHs from industrial waste is less as compared to synthetic solution, because industrial waste contained various types of pollutants like metals, azo dyes and many others compete with the selected PAHs for adsorption on the surface of adsorbents, respectively.

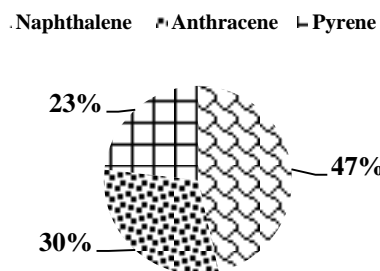


Fig. 10. Concentration of PAHs in incinerator fly ash

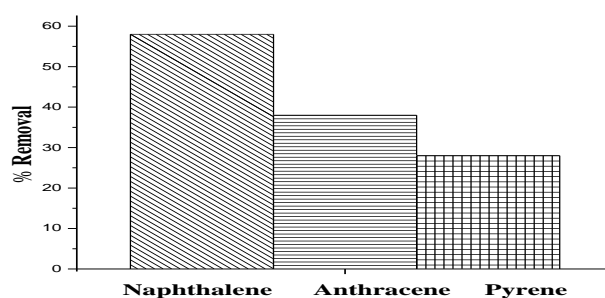


Fig. 11. Competitive (%) removal of PAHs from incinerator fly ash

5. Adsorption kinetics and isotherms

Kinetic study of the adsorption process gives an important insight to understand the mechanism. The present study is an attempt to understand the adsorption rate and sorption capacity. Different kinetics models were applied to explore the best fit one. Pseudo-second order is best fitted to explain the adsorption of naphthalene, anthracene and pyrene (see table 2). To conduct the isotherm studies, two models (Freundlich and Langmuir) were applied. The isotherm study indicates how adsorbate molecules are distributed between solid and liquid describing single or multilayer adsorption phase. Freundlich isotherm is best fitted on experimental data. Adsorption parameter of polyaromatic hydrocarbons onto synthesized alumina hybrids is tabulated in table 3.

Table 2 Kinetics parameters for the adsorption of Naphthalene, Anthracene and Pyrene on alumina hybrids

Kinetic models	q _e (calculated) mg/g	K ₁ (min ⁻¹)	R ²
Naphthalene			
First order	1.7328	-0.047x	0.8708
Pseudo – first order	1.9307	0.0041x	0.8838
Pseudo – second order	3.2886	10.055x	0.9994
Intra-particle diffusion	1.9312	0.0449x	0.839
Anthracene			
First order	1.8405	-0.0034x	0.0791
Pseudo – first order	2.7678	8E-05x	0.0818
Pseudo – second order	3.2886	10.055x	0.9994
Intra-particle diffusion	1.9896	0.0007x	0.0565
Pyrene			
First order	1.6573	-0.0355x	0.8423
Pseudo – first order	2.0663	0.0042x	0.8013
Pseudo – second order	0.3288	7.0753x	0.9983
Intra-particle diffusion	1.9831	0.0097x	0.9013

Table 3: Adsorption isotherm of Naphthalene using alumina based hybrids at induced concentration (0.001 mg/l)

Freundlich isotherm				Langmuir isotherm		
Adsorbents	qe (calculated) mg/g	K ₁ (min ⁻¹)	R ²	qe (calculated) mg/g	K ₁ (min ⁻¹)	R ²
Naphthalene						
Alumina Hybrid	1.2085	-0.814x	0.9626	0.0741	-0.8217x	0.862
Anthracene						
Alumina Hybrid	0.4928	0.1926x	0.9989	0	0	1E-13
Pyrene						
Alumina Hybrid	1.136	-0.122x	0.9924	645.28	-70.188x	0.9492

6. Conclusions

The present study showed that alumina hybrid is mesoporous material (27-33nm) with amorphous nature. The surface of adsorbent adhere with different distinct functional groups (-OH, C-H, Al-O and Al-O-Al) which are likely to be participates in binding of polyaromatic hydrocarbons. Remedial power of alumina hybrid towards naphthalene (68%), anthracene (65%) and pyrene (28%) is vary with the complex molecular structure. Pseudo-second order and Freundlich isotherm is well fitted on experimental data (R² o.999).

Recommendation: Series of alumina hybrid can be synthesized varying the organic group i.e., indole, acetanilide, phosphine for the remediation of organic and inorganic pollutants.

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Reference

- [1] S. Gan, E. Lau, H. Ng, Journal of Hazardous Materials, **172**(2), 532 (2009).
- [2] E. Ferrarese, G. Andreottola, I. A. Oprea, Journal of Hazardous Materials, **152**(1), 128 (2008).
- [3] Y. Zhang, S. Tao, Atmospheric Environment, **43**(4), 812 (2009).
- [4] V. K. Gupta, et al., Rsc Advances **2**(16), 6380 (2012).
- [5] S. Lamichhane, K. B. Krishna, R. Sarukkalige, Chemosphere, **148**,. 336 (2016).
- [6] S. Bibi, et al., Materials Science and Engineering: C, **46**, 359 (2015).
- [7] E. Euvrard, et al. Grafted cellulose for PAHs removal present in industrial discharge waters. in EGU General Assembly Conference Abstracts. 2014.
- [8] Y. Li, B. Chen, L. Zhu, Bioresource technology, **101**(19), 7307 (2010).
- [9] X. Li, et al., Journal of Environmental Engineering, **138**(9), 940 (2012).
- [10] W. Zhang, Y. Sun, L. Zhang, Industrial & Engineering Chemistry Research **55**(48), 12398 (2016).
- [11] A.A. Yakout, et al., Carbohydrate polymers, **148**, 406 (2016).
- [12] R.-W. Hsu, H.-L. Liao, P.-C. Wang. Removal of aqueous metals from wastewater using porous functional heterocyclic aromatic amines. in Nano/Micro Engineered and Molecular Systems (NEMS), 2016 IEEE 11th Annual International Conference on. 2016. IEEE.

- [13] M. E. Mahmoud, N.A. Fekry, M.M. El-Latif, *Chemical Engineering Journal* **304**, 679 (2016).
- [14] A. O. Alade, O.S. Amuda, B.I. Adekunle, Isothermal studies on adsorption of acenaphthene on activated carbon obtained from rice husk. 2012.
- [15] Y.-C. Lin, et al., *Journal of Industrial and Engineering Chemistry*, **44**, 60 (2016).
- [16] S.-H. Lin, et al., *Journal of Polymer Research*, **23**(3), 1 (2016).
- [17] M. Wähländer, et al., *Polymer* **55**(9), 2125 (2014).
- [18] R. Rogojan, et al., *UPB Buletin Stiintific, Series B: Chemistry and Materials Science* **73**(2), 67 (2011).
- [19] J. Zhou, et al., *ACS applied materials & interfaces* **4**(4), 2174 (2012).
- [20] A. Nasiri, et al., *Experimental thermal and fluid science* **35**(4), 717 (2011).
- [21] B. J. Saikia, G. Parthasarathy, *Journal of Modern Physics* **1**(04), 206 (2010).
- [22] A. Boumaza, et al., *Journal of solid state chemistry* **182**(5), 1171 (2009).
- [23] W. Xue, et al., *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **67**(3), 1030 (2007).
- [24] P. P. Nampi, et al., *Dalton Transactions* **39**(21), 5101 (2010).
- [25] A. A. El-Amir, et al., *Journal of Environmental Management* **183**, 121 (2016).
- [26] K. Parveen, et al., *Desalination and Water Treatment* **57**(1), 161 (2016).
- [27] S. Li, et al., *Environmental Science: Processes & Impacts* **15**(6), 1130 (2013).
- [28] Y. Sun, et al., *Chemistry—An Asian Journal* **8**(11), 2755 (2013).
- [29] R. Abu-Ellella, et al., *Desalination and Water Treatment* **51**(16-18), 3472 (2013).
- [30] B. Ma, et al., *Ecotoxicology and environmental safety*, **125**, 55 (2016).
- [31] F. M. T. Luna, et al., *Industrial & Engineering Chemistry Research* **55**(29), 8176 (2016).
- [32] J. Liu, et al., *Journal of Industrial and Engineering Chemistry*, **20**(2), 616 (2014).
- [33] S. Yakout, A. Daifullah, S. El-Reefy, *Adsorption Science & Technology* **31**(4), 293 (2013).
- [34] M. Anbia, M. K. Rofouei, S. W. Husain, *Chinese journal of chemistry* **24**(8), 1026 (2006).
- [35] M. Rakowska, et al., *Environmental Toxicology and Chemistry* **32**(2), 304 (2013).