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Synthesis of Ni based metal organic frameworks and its applications for removal of polyaromatic hydrocarbons

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ABSTRACT: Metal Organic Frameworks (MOFs) are widely employed as catalysts and semiconductors due to unique combination of crystalline and porous structure. The presence of polar and non-polar groups on organic linkers provides extra coordination sites for attachment of various metals. The topology of single and mixed organic ligands is tuned to higher surface area and increased porosity likely to serve as good adsorbents.

The present study is based on synthesis of single and mixed ligand MOFs with Nickel as precursor. Oxalic and trimesic acid, representatives of di- and tri- carboxylates provides the organic framework. The characterization of synthesized MOFs by FTIR, XRD and SEM/EDX techniques reveal average crystallite size (0.2-3nm) and Ni is incorporated to mass percentage of 9-13%. Ni-O binding is exhibited at FTIR frequency of 493-500cm^{-1}. The application of synthesized MOFs in batch experiment at varying adsorbent dose, concentration and temperature demonstrated adsorptive capacity for Polyaromatic hydrocarbons in the sequence dibenzofuran (81%) > phenanthrene (91%) > anthracene (33%). The adsorbents were also proven to be effective for removal of pollutants from industrial waste with average percent removal of 73% for incinerator ash.

The study concluded that use of synthesized MOFs as an adsorbent for removal of pollutants is most effective way for environmental remediation. These MOFs can also be applied for catalysis of toxic environmental pollutants.

KEYWORDS: Oxalic acid, Trimesic acid, Dibenzofuran, Phenanthrene, Anthracene.

1 INTRODUCTION

The continuous industrial discharge and accumulation of environmental pollutants has impacted almost every aspect of life forms and physical compartments of the environment. The toxic and persistent nature of many of the pollutants poses a threat and their removal from environmental components is even more challenging [1]. To combat these problems, the researchers are continuously urging for effective and economically viable remedial measures.

Upto now various conventional methods have been adopted for removal of environmental pollutants. Of these, adsorption offers an easy, low cost and effective alternate process. Its preference is owned by the versatility and regeneration of adsorbents. However, limited numbers of structural and porous architectures available for sorption limit the usage [2] of well established adsorbents like Activated carbon and zeolites. So, research is directed at the synthesis and development of novel adsorbents with flexible artifacts.

Metal Organic Frameworks (MOFs) represent class of hybrid material that exist as infinite crystalline lattices with metal clusters and organic linkers, and possess accessible cages, tunnels and modifiable pores [3]. These properties render MOFs as efficient adsorbents for diverse applications [4]. Further, substitution of polar or non polar groups on organic backbone [5] makes them more selective (due to enhanced hydrophilicity and hydrophobicity) for efficient removal of hazardous compounds. MOFs have been successfully explored as sorbents [6]. For this purpose, various types of MOFs have been synthesized with variations in central metal, organic linkers and incorporated active species. However, limited use of MOFs [7] has been reported in the removal of polyaromatic hydrocarbons. Poly aromatic hydrocarbons (PAH) belongs to Persistent Organic pollutants are released naturally from forest fires and volcanic eruptions but human activities have increased their amount in environment by incomplete pyrolysis of fossil fuels such as coal and other organic substances at domestic and industrial level. Due to their long half life PAH are considered as one of the most toxic classes of pollutants and their removal from environment is mandatory **[8].**

The present research is an attempt to synthesize novel MOFs with variation of single and mixed ligand and incorporation of Ni as metal. These MOFs were further evaluated for removal of linear, non linear and substituted polyaromatic hydrocarbon.

2 MATERIAL AND METHODS

Hydrothermal method [9] was adopted for synthesis with slight modification. A greener aspect was added by carrying out the synthesis under ambient temperature and pressure conditions. Further, novelty of mixed ligands (di- and tri-carbooxylate) synthesis of MOFs is also introduced. Oxalic acid and trimisic acid were used to provide organic framework for the incorporation of nickel metal. The synthesis method follows the general procedure as:

Each of the Carboxylic acid (2mmol) dissolved in absolute ethanol (12ml) was added separately, to aqueous Ni-salt solution (4mmol) under continuous stirring for 30 minutes. The solution was left undisturbed for nucleation in fume hood for 5 days. The resultant product was filtered, washed repeatedly with ethanol, and evaporated on rotary evaporator. The dried product was pulverized and placed in desiccator till further use. In a similar fashion, mixed ligand MOFs was synthesized by adding 1:1 mixed solution of oxalic and trimesic acids to the stirring solution of metal salt.

The synthesized materials were characterized for surface and bulk properties on standardized FTIR (FTIR 8400, Shimadzu, Japan), X-rays Diffraction (Panalytical X'Pert Pro multipurpose) and SEM/EDX (JEOL JSM-6490, Japan).

The adsorptive potential of synthesized single and mixed ligand MOFs for removal of selected PAH was evaluated in batch adsorption experiment on UV-Visible spectrophotometer (UV-1601-Schimadzu, Japan) under varying conditions. Each batch was administered with three induced PAH concentration of (0.001mg/L, 0.003mg/L, 0.005 mg/L) on each of the adsorbent dose (1mg, 5mg, 10mg) and working temperatures of 25°C (room temperature), 50°C, and 70°C. The absorbance of Phenanthrene, Anthracene, and Dibenzofuran was recorded at 250nm, 375nm and 292nm, respectively after full spectral scan. The adsorption (percentage removal) was calculated from the constructed standard calibration curve using the formula as.

$$\%R = \frac{Ci - Ct}{Ci} \times 100$$

3 RESULTS AND DISCUSSION

The present research provides an efficient, simple and environment friendly greener method for the successful synthesis of uni-and bi-ligand organic framework centralized around Nickel. Further, the efficacy of each of the synthesized material as adsorbent under varying experimental batch conditions is determined.

3.1 CHARACTERIZATION OF SYNTHESIZED MATERIALS

The synthesized products were characterized using FTIR, XRD and SEM/EDX to identify its bonding, crystallinity, morphology and elemental composition. FTIR analysis (see Figure 1) indicated the presence of organic ligand in (NiOX) at 721cm^{-1} that may be attributed to structural vibration of C-C bond. The peak at 829cm^{-1} and 1300cm^{-1}-1370cm^{-1} is assigned to asymmetric stretching and symmetric vibration of υ(CO), respectively, in oxalic acid. The incorporation of metal (Nickel) into organic frame depicts sharp and intense asymmetric stretching modified to broad band at 1710cm^{-1}-1780cm^{-1}. This change might be representation of υ(OCO) due to metal binding [10].

FTIR spectrum (see Figure1) of Ni-trimesic acid (NiT) reveals the sharp peak of C-H in-plane and out-planes bending vibration of benzene ring [11] at 1150cm^{-1}-1250cm^{-1} and 675-900cm^{-1}. On the other hand, bi-ligand Ni-MOF (NiTOX) showed C-H in plane bending in the range 1278cm^{-1}-1107cm^{-1}, whereas, C-C stretching of benzene ring is depicted at 1404cm^{-1} - 1468cm^{-1}. In- plane bending vibration of υ(CO) is represented by two sharp peaks in the range 650cm^{-1} -750cm$^{-1.}$ Ni-O coordination bond determined at 400-500cm^{-1} represents binding of metal with organic ligand [12].

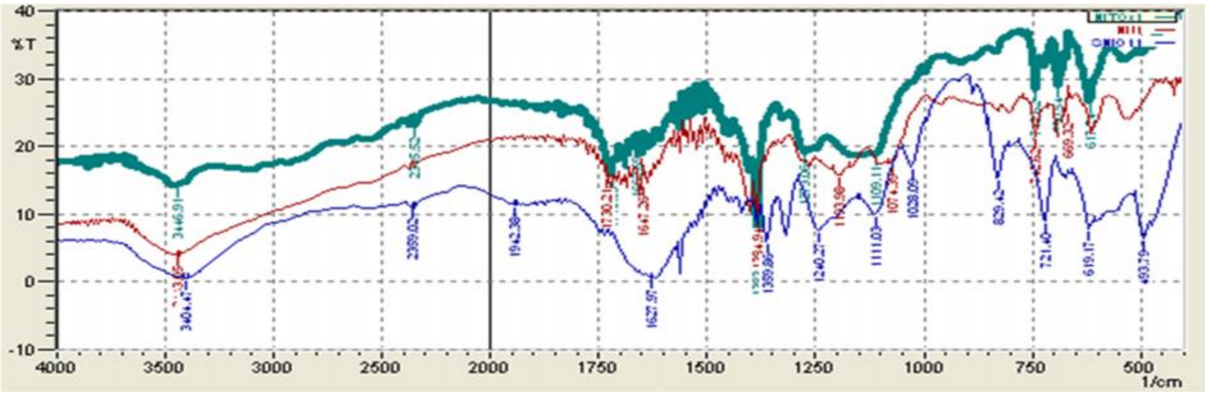
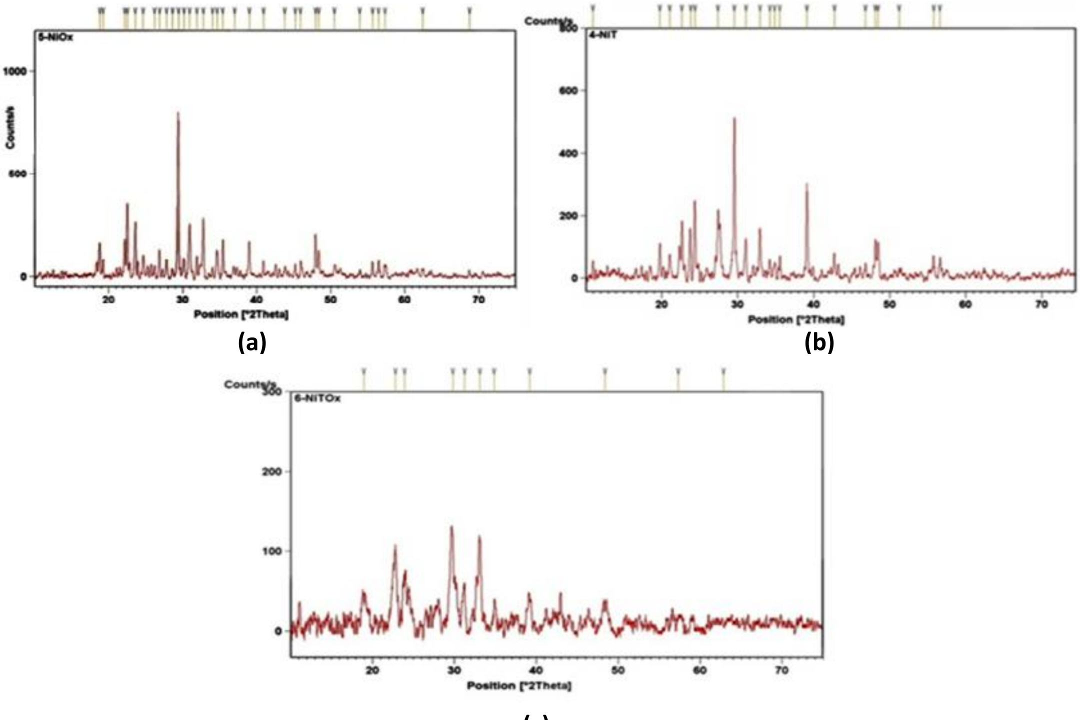


Fig. 1. FTIR Spectra of Ni based uni-and bi-ligand MOFs (a) NiOX (b) NiT (c) NiTOX

The synthesized metal-organic materials were impinged with X-rays to determine diffraction of incoming rays at definite angles by inter-spacing of layers/planes (see Figure 2). Ni doping on oxalic acid (NiOX) shows sharp and intense peaks at 18.8^{o}, 22.5^{o}, 23.6^{o}, 29.4^{o} and 30.9^{o} with d spacing 4.7A^{o}, 3.9A^{o}, 3.7A^{o}, 3.0A^{o} and 2.8A^{o}, respectively. Similar pattern was observed by Rios, et al., 2012. However, emergence of small peaks diffracted at 38.9^{o} and 47.9^{o} may indicate unreacted NiO as impurity (Haq and Haider, 2010). On the other hand, Nickel based trimesic acid (NiT) revealed important diffractions at 19.7^{o}, 24.3^{o}, 27.4^{o}, 29.5^{o}, 32.9^{o} and 39.0^{o}. Furthermore, diffraction due to –COOH is observed at lower angles (18.8^{o} and 19.7^{o}) indicating presence of two and three groups attached to aliphatic (oxalic acid) or aromatic (trimesic acid), respectively (Yang, *et al.,* 2014). The expected metal binding through carbonyl group is demonstrated at angle of 29^{o}-31^{o}. However, it is interesting to note that aliphatic binding diffracts with high intensity (close to 100) in comparison to aromatic groups

The composite (NiTOX) synthesized by mixing equimolar ratio of aliphatic (oxalic) and aromatic (trimesic) offers unique diffraction pattern. It exhibits metal to carbonyl linkage in the range 29^{o}-31^{o}. It is also noted that a new peak at 33.1^{o} of high intensity appeared as a result of aliphatic to aromatic linkage. In addition, diffracted peaks due to free –COOH aliphatic and aromatic groups diminishes in the composite. This confirms the successful synthesis of composite having both reagents.

XRD pattern may conclude that the product is crystalline in nature. The crystalline nature of MOFs is reported in the literature [3].



(a)

(b)

(c)

Fig. 2. XRD of synthesized Ni-based MOFs (a) NiOX (b) NiT (c) NiTOX

Each of the synthesized Metal Organic Framework was scanned under SEM for surface morphological features and assessment of average particle size. The micrographs are reproduced in Figure 3.

The basic organic framework of oxalic acid and trimesic acid complexed with Nickel shows beautifully arranged particles with well defined geometrical shapes. Agglomerates of cubic shapes stacked one above other defines NiOX, whereas, the same cubic geometry is more clearly attained by NiT particles. It might be attributed to the available three –COOH groups attached to aromatic ring for the later in comparison to two aliphatic in the earlier. It is suggested that higher is the number of binding groups, more regular geometrical arrangement is attained. Cubic geometry with tetrahedral arrangement for Ni-Oxalate is reported by [10]. The composite (NiTOX) exhibits agglomerates of cubes and pure cubic pattern, representing participation of both components. Further, conversion into the composite is verified by overwhelming appearance of new phase (showing interconnected cage like structure) widely seen in the image. The synthesis of such composite is the peculiar feature of the present research and not reported elsewhere.

The size determined by SEM for NiOX (1-5µm) is found slightly smaller than NiT (1.47-6µm) crystals. Whereas, composite NiTOX size is diversified over the range 24-840 nm. The study concludes that synthesized MOFs are mesoporous with definite crystalline geometry. Such characteristics features are also identified in the literature [14] for MOFs.

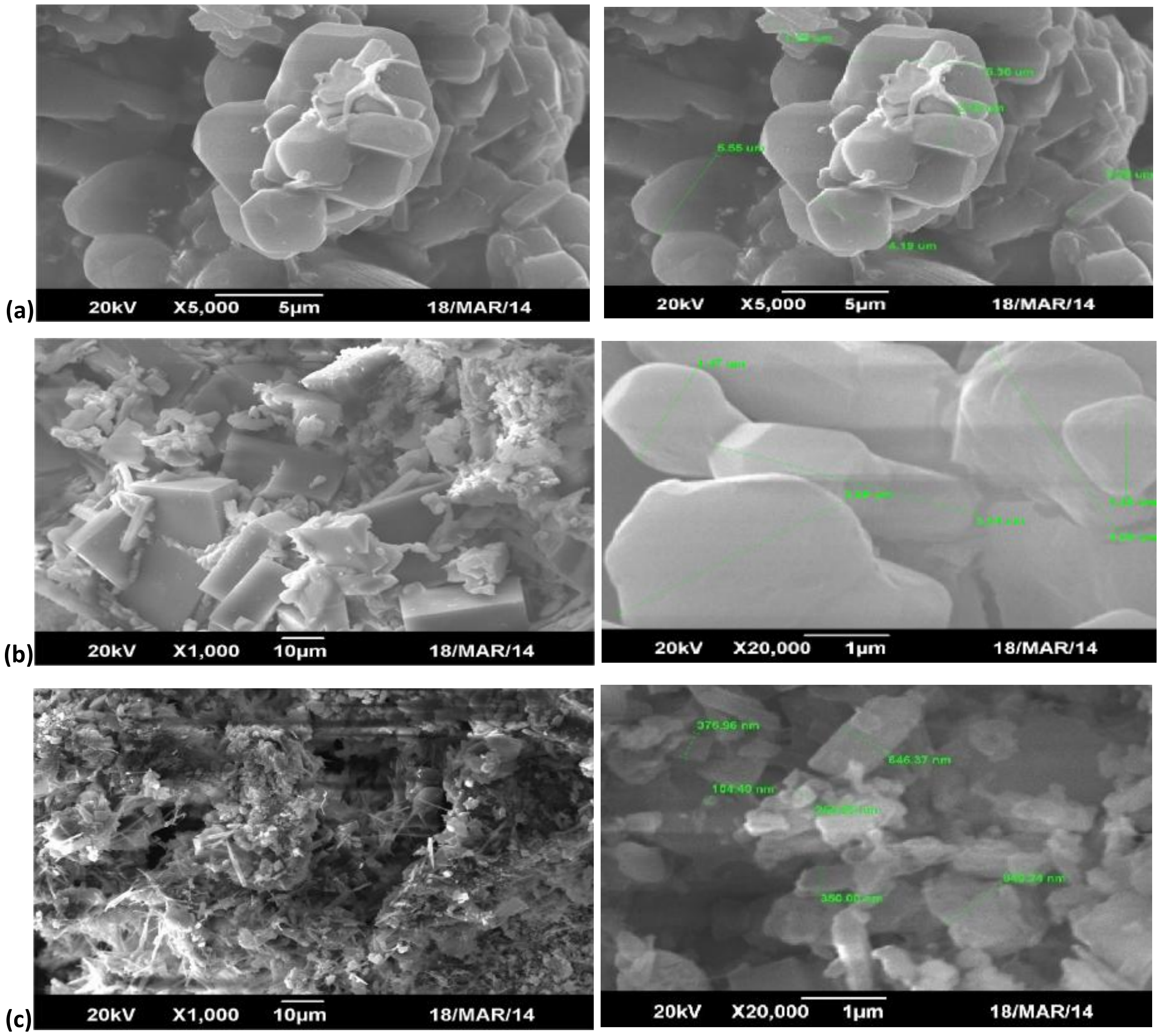


Fig. 3. SEM images of synthesized Ni-based MOFs (a) NiOX (b) NiT (c) NiTOX

The incorporation of metals into the organic framework was determined by EDX analysis. Highlights of results (given in Table 1) clearly indicates carbon and oxygen as the main constituents of each synthesized material confirming the framework (of oxalic acid and trimesic acid) is constructed mainly on these two atoms. However, variation in carbon content in NiOX and NiT can directly be related to less and more carbons in aliphatic ($C_2H_2O_4$) and aromatic ($C_9H_6O_6$), respectively. Further, carbon to oxygen ratio in the respective two MOFs (11.4:1.3) indicates more oxygen for less carbon containing compound, supported by molecular formulae. The mixed ligand composite shows carbon to oxygen ratio as 1:2, also supported by [15].

Table 1. EDX data of Ni-based uni-and bi-ligand MOFs

Sample Code	NiOX			NiT			NiTOX		
	Atom (%)	**Mass (%)**	**Error (%)**	**Atom (%)**	**Mass (%)**	**Error (%)**	**Atom (%)**	**Mass (%)**	**Error (%)**
C	7.26	4.36	6.75	41.79	30.67	3.86	31.07	22.98	3.20
O	57.85	44.99	4.65	53.45	52.24	10.10	65.46	64.49	6.97
Ni	4.58	13.06	15.42	4.76	17.09	26.15	3.46	12.52	22.69

3.2 APPLICATION FOR REMOVAL OF PAPS

Adsorption removal experiments were conducted on phenanthrene, anthracene and dibenzofuran to study the adsorption behavior of synthesized adsorbents for removal of POPs. The results indicated better adsorption for phenanthrene and dibenzofuran than anthracene. The reason for good adsorption of phenanthrene than anthracene could be due to more hydrophilic nature of phenanthrene than anthracene which allows better interaction with hydrophilic adsorbents due to hydrogen bonding and thus adsorption is enhanced [16]. Further, the non linear structure of phenanthrene favors more adsorption in small pores than the linear anthracene. In case of dibenzofuran, adsorption is more due to presence of oxygen atom in the ring structure which makes it more electronegative and behaves as anion. This anionic behavior gives it more opportunity to adsorb on the cationic surface due to acidic nature of adsorbents [17].

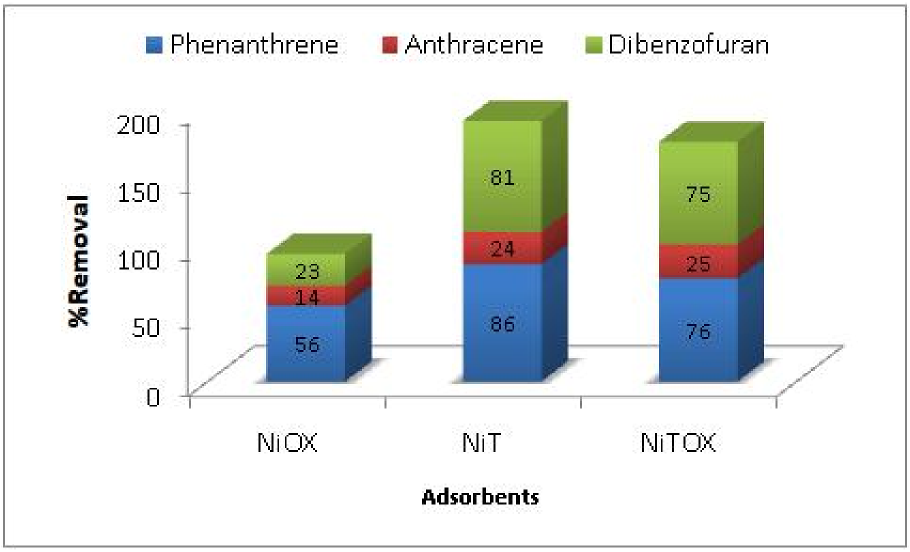


Fig. 4. Efficiency of synthesized MOFs as adsorbents for removal of PAH

3.2.1 EFFECT OF CONTACT TIME

Batch adsorption experiment was conducted to study the effect of contact time on removal efficiency of POPs (phenanthrene, anthracene and dibenzofuran). The purpose of studying contact time was to establish the equilibrium reaction time between adsorbate and adsorbent. Results are graphically presented in Figure. It is seen that the rate of phenanthrene uptake by all adsorbents was initially quite high, followed by much slower subsequent removal rate leading to equilibrium. The equilibrium attained in 10-15min which further results in desorption phenomena. The rapid approach of equilibrium could be due to presence of external adsorption sites which are easily accessible for these adsorbents [18].

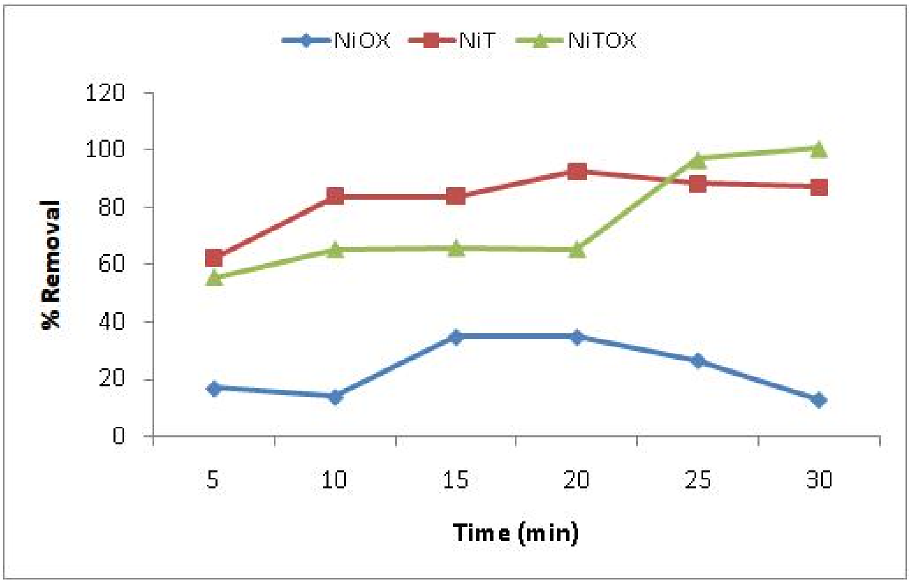


Fig. 5. Removal (in Percentage) of phenanthrene with time

3.2.2 EFFECT OF ADSORBENT DOSE

To identify the effect of adsorbent dose on adsorption behavior of Phenanthrene, batch experiments was conducted on three doses (1mg/Kg, 5mg/Kg and 10mg/Kg) with varying initial concentrations(0.001mg/L, 0.003mg/L and 0.005mg/L. The results presented in Figure 3.2.2.2 showed no specific trend. Most of the adsorbents presented decrease in adsorption with increasing dose due to aggregation of adsorbent particles.

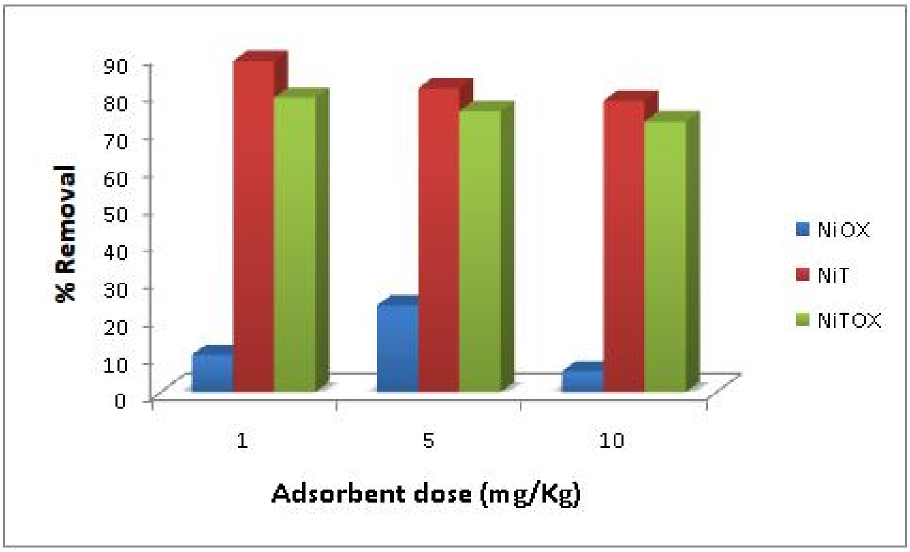


Fig. 6. Effect of adsorbent dose for removal of phenanthrene

3.2.3 EFFECT OF INITIAL CONCENTRATION

Effect of induced concentration for removal of phenanthrene was studied for induced concentrations of 0.001mg/L, 0.003mg/L and 0.005mg/L (Figure 3.2.2.3). The adsorbent NiOX and NiT presented decreased in concentration with increasing the initial concentration while NiTOX showed irregular trend.

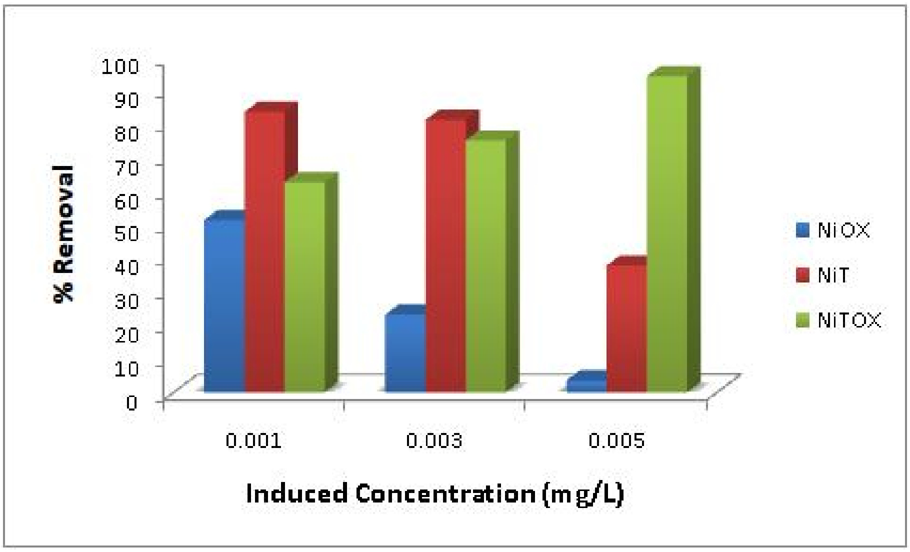


Fig. 7. Effect of induced concentration for removal of phenanthrene

3.2.4 EFFECT OF TEMPERATURE

Effect of temperature for removal of phenanthrene was studied at 25°C, 50°C and 70°C with optimum initial concentration of 0.003mg/L and adsorbent dose of 5mg/Kg. The results presented in Figure 3.2.2.4 presented the maximum adsorption at 50°C which indicates that removal of phenanthrene requires specific activation energy. This activation energy creates more reactive sites by decreasing the density and hence increases the rate of reaction. Less adsorption at 70°C may be result of increase in kinetic energy of molecules which hinders the adsorption process.

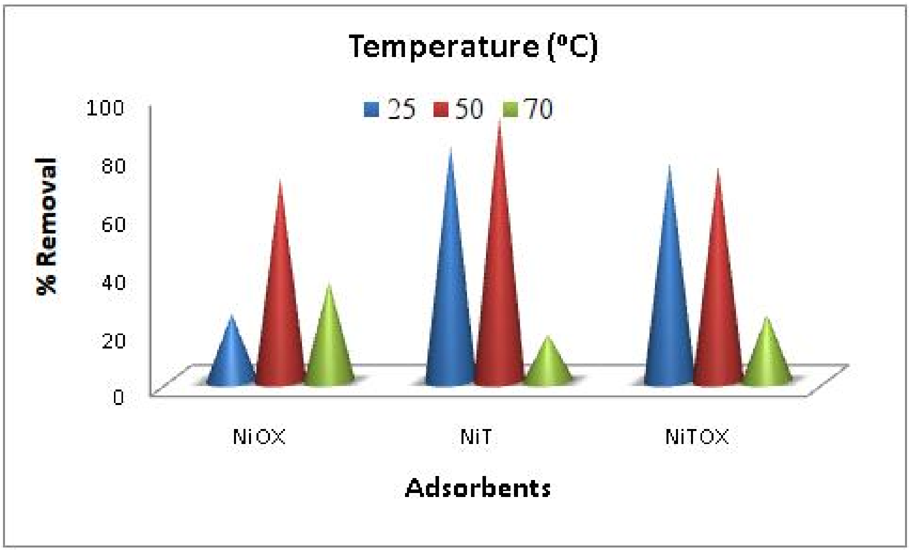


Fig. 8. Effect of temperature for removal of phenanthrene

3.2.5 REMOVAL EFFICIENCY OF DIFFERENT ADSORBENTS

Effect of different adsorbents on percent removal of phenanthrene was studied by taking the optimum concentration i.e. 0.003mg/L and adsorbent dose i.e. 5mg. The percentage removal of PAH increased in the following increasing order i.e. NiOX < NiTOX < NiT. This trend could be due to presence of more functional groups of carboxylic and phenolic in NiT and NiTOX as compared to NiOX. The results also presented no effect of type of metal present in MOFs for removal of phenanthrene.

3.2.6 ADSORPTION ISOTHERM AND KINETICS

Kinetic study of the adsorption gives an important insight to understand the mechanism of adsorption. The adsorption kinetics and isotherm models were applied on batch experiments for removal of phenanthrene. Equilibrium Isotherms are used to quantify the adsorptive capacity of three adsorbents while kinetic data is used to predict the rate at which the adsorbates are removed from the solution. Isotherm studies were conducted using three models i.e. Freundlich, Langmuir and Temkin. The isotherm studies indicated that the adsorption of all pollutants followed the Freundlich and Temkin model. In order to investigate the sorption kinetics of pollutants, first order, pseudo first order, pseudo second order and intra-particle diffusion were applied to fit the experimental data. The results indicated the pseudo second order the best fit model to explain the adsorption kinetics.

Table 2. Adsorption isotherms of PAH

Dyes	Adsorbent	Isotherm Models								
		Freundlich			Langmuir			Temkin		
		K_F	n	R^2	K_L	q_m	R^2	K_T	B_1	R^2
Phenanthrene	NiOX	-4.057	6.886	0.990	-11.96	49.18	0.993	-7.833	7.054	0.999
	NiT	-1.467	2.529	0.999	-0.783	6.422	0.967	-11.98	9.935	0.999
	NiTOX	-1.448	2.500	0.998	-0.760	6.315	0.993	-12.14	10.03	0.999
Anthracene	NiOX	-2.810	4.509	0.845	40.19	-9.032	0.910	6.757	-7.598	0.681
	NiT	1.040	-3.402	0.917	-19.59	10.49	0.882	-3.525	4.396	0.977
	NiTOX	0.537	-1.817	0.935	-3.321	2.706	0.959	-3.834	4.641	0.998
Dibenzofuran	NiOX	-1.637	2.760	0.993	-1.086	8.030	0.974	-11.37	9.585	0.999
	NiT	-1.226	2.191	0.999	-0.474	4.83	0.998	-13.85	11.07	0.997
	NiTOX	-1.365	2.383	0.998	-0.644	5.735	0.995	-12.70	10.38	0.999

Table 3. Kinetic models of PAH

Dyes	Kinetic Models						
	Adsorbent	Pseudo-2nd order			Intra-particle		
		K_2	q_e cal	R^2	A	K_{id}	R^2
Phenanthrene	NiOX	2.690	-3.813	0.966	-0.007	1.304	0.649
	NiT	0.534	0.047	0.996	-0.001	1.823	0.306
	NiTOX	0.534	-0.065	0.997	-0.001	1.832	0.139
Anthracene	NiOX	2.625	7.946	0.940	-0.003	1.099	0.031
	NiT	0.900	3.582	0.913	0.019	1.045	0.710
	NiTOX	0.853	2.269	0.905	-8E-05	1.529	0.000
Dibenzofuran	NiOX	0.772	-0.606	0.934	-0.008	1.859	0.474
	NiT	0.434	-0.353	0.971	-0.002	1.972	0.247
	NiTOX	0.479	-0.385	0.950	-0.000	1.888	0.030

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