



Synthesis of β -Octabromo Meso-Tetracycloheptyl Porphyrinogen and its Application in Arsenic Removal

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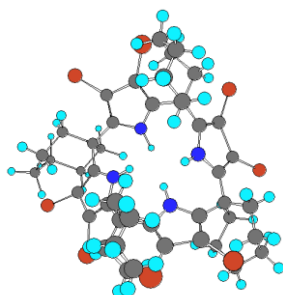
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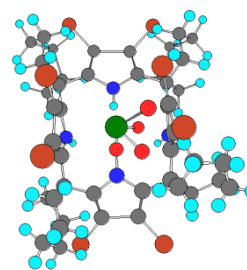
ABSTRACT

Synthesis of β -Octabromo meso-tetracycloheptyl porphyrinogen(Br-mtcp) has been achieved by a simple method and characterized. Considering their host-guest binding capacity, Br-mtcp was tested for removal of arsenic by batch mode. Arsenic bound compound was characterized by NMR, FT-IR, SEM and XRD that confirms the interaction of arsenic with the adsorbent. Important physico-chemical parameters like contact time, concentration and pH were investigated. Three kinetic models were studied among which pseudo 2nd order best describes the mechanism of arsenic uptake with R^2 value of 0.999. Maximum adsorption was found to be 16.52mg/g. Freundlich isotherm was found to follow best with R^2 value 0.999. Field samples were collected from nearby areas in Ranchi and detoxified to a good extent.

Graphical Abstract



Before Adsorption



After Adsorption

Highlights

- Synthesis of β - octabromo meso-tetracycloheptyl porphyrinogen.
- Characterization using FTIR, XRD, SEM and NMR.
- Arsenic removal by synthesized porphyrin based ligand.
- Batch study of adsorption of arsenic onto the synthesized ligand.
- Real water sample analysis for arsenic removal in Ranchi city.

Keywords: β -octabromo meso-tetracycloheptyl porphyrinogen, XRD, arsenic removal, kinetic, isotherm.

INTRODUCTION

Arsenic contamination is becoming a global threat since it is one of the most toxic element to health and humanity [1]. A large number of industries starting from petroleum, chemical, refineries, power plants etc results in arsenic contamination in water resources. Arsenic contamination occurs due to natural calamities like volcanic eruptions, weathering, and other bioactive reasons [2], also there were several anthropogenic factors responsible for this which includes smelting, refining, extensive use of fertilizers and burning of fossil fuels [3, 4]. Inorganic arsenic is more toxic than organic arsenic [5, 6]. Acute arsenic poisoning leads to cardiomyopathy, hypertension, neuropathy, hepatitis and dysfunction of liver enzymes. However chronic exposure affects vascular and cardiovascular system [7]. As (III) and As (V) have ability to bind both with organic and inorganic components in nature and human body [7, 8]. Recommended concentration of arsenic is 10 µg/L [9]. A large number of treatment methods including ion exchange [10], co-precipitation [11], sorption techniques [12] were applicable in removal process. Pyrrole based ligand was seen to be effective for removal of arsenic from contaminated water particularly due to their receptor sites for anionic and neutral guest species related to NH array present in the molecule [13]. Synthetic adsorbents for removal of toxic ions from contaminated water was reported previously which includes synthesized oxide [14], porphyrinogens[15], and N-methylglucamine derivative of porphyrinogens [16]. There is an urge to prepare anion binding agents, which can be easily synthesized with low cost and less time by using selective substrates. J.L. Sessler and co-workers are previously reported the conformational features and anion (like Cl⁻, Br⁻, F⁻) binding properties of porphyrinogens. [17-22].

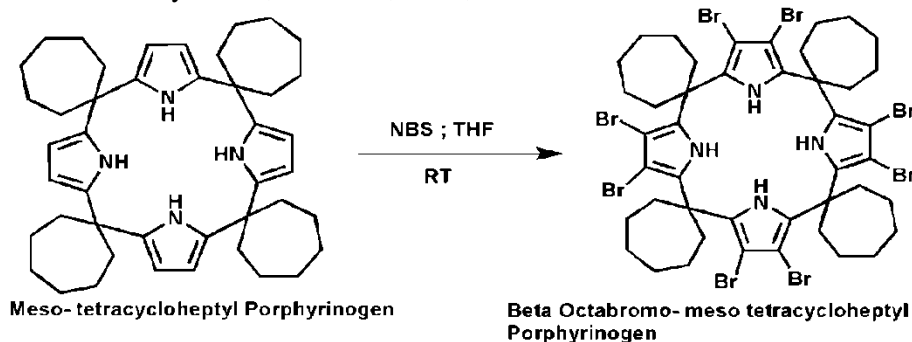
The present work reports the synthesis of Br-mtcp and its binding with arsenate ion. The investigation was carried out at optimal conditions taking into account respective batch adsorption parameters – contact time, pH, concentration, kinetics and isotherm study. Real water sample analysis evaluated the significance of the material on industrial scale and error analysis was done to obtain better accuracy of experimental data.

MATERIALS AND METHODS

Chemicals and materials: Freshly prepared stock solutions of arsenic salt (Na₂AsHSO₄·7H₂O), freshly distilled Pyrrole(98%), Cycloheptanone, N-Bromo succinimide from Sigma Aldrich were used. THF, Acetone, Methanol, Chloroform and triethylamine were received from Fisher Scientifics and SDDC from Acros Organics were used as received.

Synthesis of β-Octabromo meso-tetracycloheptyl porphyrinogen: The procedure involved similar mechanism as reported earlier with mild modifications [23]. Synthesis of β-substituted porphyrinogens involved the reaction of meso-tetracycloheptyl porphyrinogen with NBS in THF at room temperature and stirred for 30-40 min [24, 25]. The product Br-mtcp was obtained by solvent evaporation, washed with cold and hot water, finally recrystallized with acetone and water.

Characterization was done by FT-IR, ¹H-NMR, XRD, SEM.



Scheme 1: Synthesis of β-Octabromo meso-tetracycloheptyl porphyrinogen

RESULTS AND DISCUSSION

Characterization

FT-IR: FT-IR analysis of synthesized material indicates complete β substitution. [26]. The reactive $-\text{NH}$ group is responsible for effective binding through H-bonding (Fig 1).

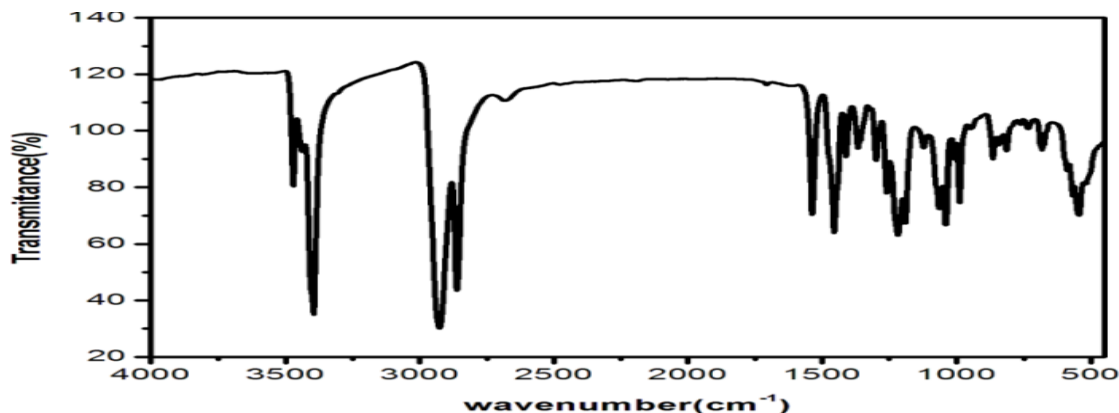


Fig 1. FTIR spectra of Br-mtcp

NMR: ^1H NMR was recorded for Br-mtcp and data is presented in table-1. N-H peak appears at 6.88 ppm (vs TMS). Peaks at 1.42 and 1.96 represent ring hydrogens of cycloheptyl group. Upon reaction with arsenic, N-H peaks were found to be shifted to 7.76 (0.88 ppm shift). This can be attributed by weak hydrogen bonding interaction of $\text{N-H}\cdots\text{H}_2\text{AsO}_4^-$. Cycloheptyl protons almost retain their peak position.

Table 1. ^1H NMR shifts of protons before and after Br-mtcp – arsenate adsorption

Proton	Br- mtcp δ (ppm)	Br-mtcpAs δ (ppm)	$\Delta\delta$ (ppm)
1	6.88	7.76	0.88
2	1.42	1.44	0.02
3	1.96	1.96	0.00

1-N-H protons, 2,3-Cyclic CH_2 -protons.

XRD: The powder XRD patterns revealed the crystalline nature of the synthesized adsorbent as shown by its sharp peaks in (A). After adsorption, crystallinity decreases indicating decrease in signal intensity (B). The difference in the spectra before and after adsorption denotes the surface interaction of the adsorbent-adsorbate system and the shifting in the peaks suggested interaction with arsenic species in the ligand as shown in Fig 2.

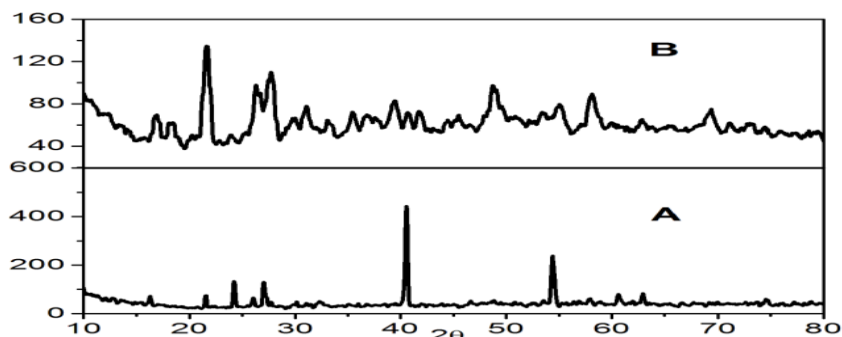


Fig 2. XRD spectra (A)-Before adsorption (B)- After adsorption

SEM: The ligand was analyzed before and after adsorption using SEM analysis (Fig 3). This suggests binding of arsenic with ligand surface. The image obtained after adsorption clearly suggested the interaction of the two species shown by its dense and compact surface.

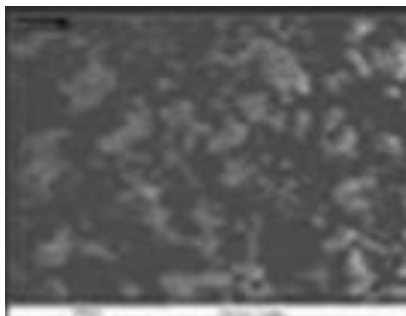


Fig. 3(a) SEM of Br-mtcp before adsorption

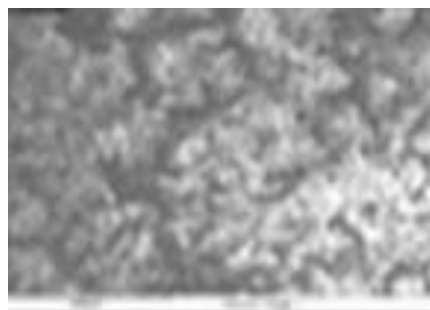


Fig. 3(b) SEM of Br-mtcp after adsorption

Adsorption studies- Batch study

Effect of contact time: The effect of contact time for removal of arsenic onto the adsorbent were seen (20-100 mins.), at 10ppm, 25°C, 120±5rpm, pH=7.2 and using 0.2g of material. Equilibrium was achieved within 60 minutes. The effect of contact time on removal of arsenic was shown in Fig 4(a).

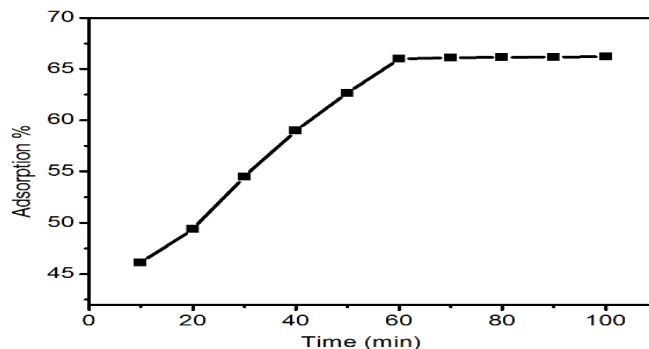


Fig 4(a) Effect of contact time on removal of As(V) by Br-mtcp at $C_0=10\text{mg/L}$, 25°C, pH = 7.2, 130rpm, dose=0.2g.

Effect of concentration: The effect of initial concentration of arsenic was investigated. The increase in adsorption percentage with increasing concentration was seen upto 8ppm. The constant removal percentage might be the result of the saturation of active receptor sites of the adsorbent surface for the effective binding with the metal ion species (Fig 4 (b)).

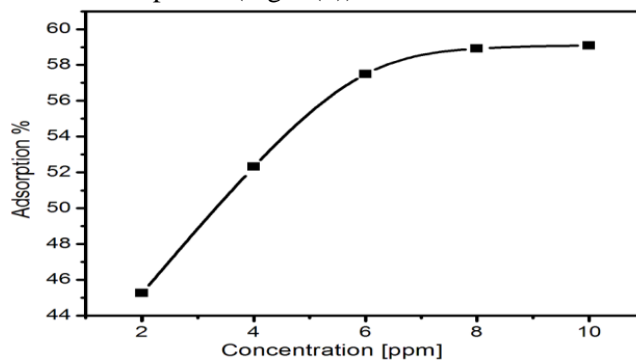


Fig. 4(b) Effect of initial concentration on the removal of As (V) species by Br-mtcp at $C_0=10\text{ppm}$, 25°C, pH=7.2, dose = 0.2 g.

Effect of pH: The effect of pH shows the process is a pH driven process as shown in graph Fig 4(c). As the pH increases from 1-7 the adsorption percent increases with maximum adsorption at pH 7 and then decreases with increasing pH.

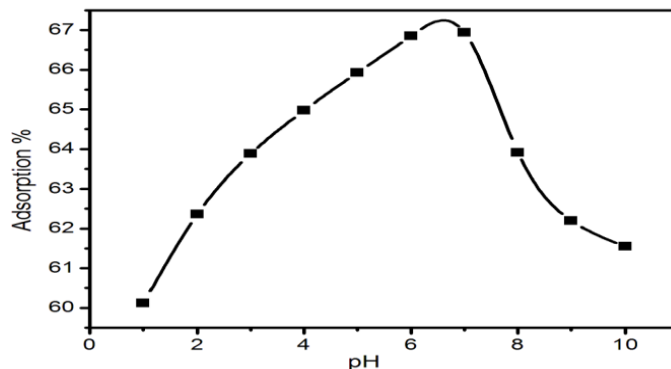


Fig. 4(c) Effect of pH on removal of As(V) by Br-mtcp at $C_0=10\text{mg/L}$, 25°C , 130rpm, dose = 0.2g.

Adsorption kinetics: Pseudo 1st order, pseudo 2nd order and intra-particle diffusion kinetics were tested and presented (Fig 5(a-c)). Table 2 shows the adsorption constants for different kinetic models. Pseudo 2nd order was found to be followed with R^2 0.999. Respective rate constant and adsorption capacity was found to be $0.700\text{ g mg}^{-1}\text{ min}^{-1}$ and 9.65 mg g^{-1} .

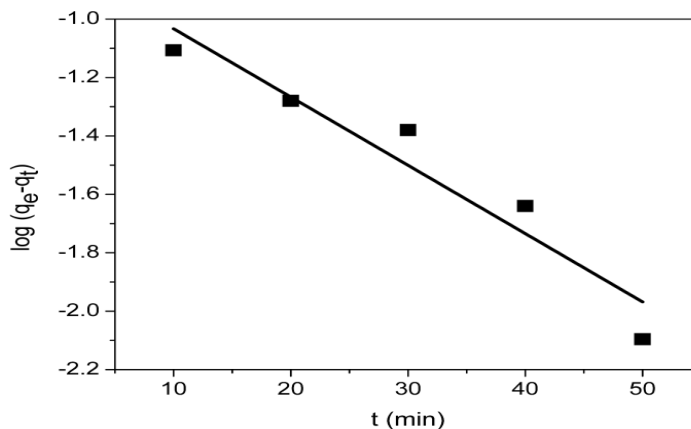


Fig. 5(a) Pseudo 1st order kinetic plot

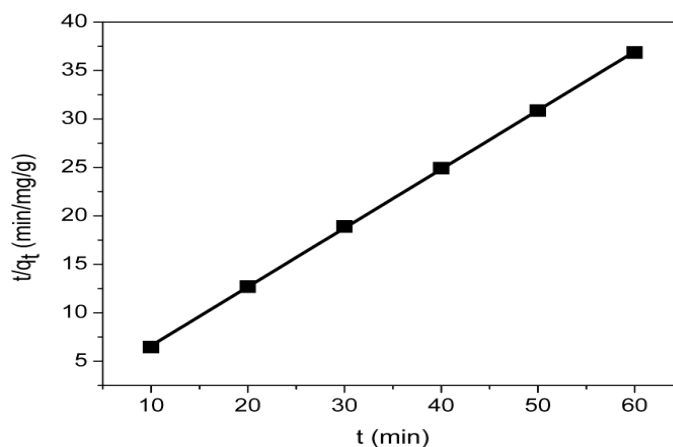


Fig. 5(b) Pseudo 2nd order kinetic plot

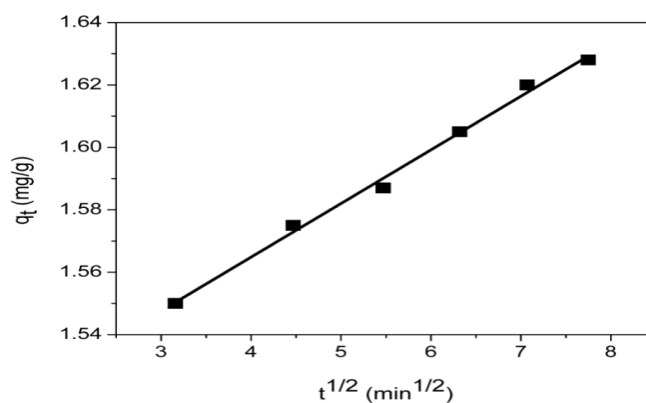


Fig. 5(c) Intra-particle diffusion kinetic plot

Table 2. Different kinetic model constants

Order	q_e (mg/g)	K	R^2
Pseudo 1 st	6.26±0.12	0.053min ⁻¹ ±0.001	0.897±0.036
Pseudo 2 nd	9.65±0.08	0.700g/mg.min±0.051	0.999±0.007
Intra-particle diffusion	1.56±0.21	0.0172mg/g.min ^{0.5} ±0.004	0.993±0.011

Adsorption isotherm: Isotherms are representations of functions of concentration at a constant temperature [27]. These suggest the type of interaction between the adsorbent – adsorbate system in terms of various isotherm constants as adsorption capacity, adsorbent intensity and regression co-efficient values. Most often two basic models namely Langmuir and Freundlich were studied to evaluate the type, nature and efficiency of the adsorbent species. Langmuir explains the nature of the surface interaction to be homogeneous while Freundlich focuses on the heterogeneity of the active sites. Table 3 displays the values of isotherm constants pertaining to the above two models. Freundlich model fits best the process with R^2 value of 0.999.

Table 3. Langmuir and Freundlich model constants for adsorbate-adsorbent system

Isotherm models	Temperature (K)		
	308	318	328
Langmuir			
b(L/mg)	0.058±0.001	0.072±0.002	0.079±0.001
q_0 (mg/g)	11.502±0.131	10.023±0.088	9.120±0.122
R^2	0.916±0.001	0.928±0.006	0.925±0.011
Freundlich			
K_F (mg/g)	0.618±0.003	0.602±0.010	0.589±0.007
n	1.829±0.002	2.123±0.050	2.516±0.120
R^2	0.999±0.002	0.998±0.001	0.994±0.010

APPLICATIONS

Real water sample analysis for removal of arsenic from Ranchi city: Arsenic is permissible upto 0.01mg L^{-1} by WHO guidelines but one of the sampling area contained maximum arsenic of about 0.2mg L^{-1} which is situated in Tunkitoli near industrial area of Kokar, Ranchi [28]. It is a semi-urban area receiving monsoons much often. About 75% removal of arsenic by the synthesized ligand was estimated. Evaluation of removal efficiency was carried out by treating wastewater contaminated with arsenic collected from affected areas in Ranchi as mentioned in Table 4.

Table 4. Arsenic removal by Br-mtcp from wastewater samples collected from different areas in Ranchi city

Site	As (initial, ppm)	As(final, ppm)	% Removal
S1	0.201	0.049	75.62
S2	0.088	0.024	72.72
S3	0.068	0.018	73.52

Sampling locations in Ranchi city

S1-Tunkitoli near kokar, S2-Near kanke dam, S3- Dhurwa (Sector 2)

CONCLUSIONS

The present investigation reports synthesis of a substituted porphyrinogen and uptake of As(V) by it at optimal experimental conditions. The efficiency of removal was optimized at various adsorption parameters like contact time, pH, concentration and kinetic models. Pseudo 2nd order kinetics best describes the mechanism of adsorption for the complexation of the ligand with the arsenic species and isotherm study follows Freundlich model. The material was found to be promising adsorbent for removal of arsenic.

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