

# EFFECT OF COMBINED MAGNETIC NANO PARTICLE AND MANNICH BASE IN PHENOLIC WASTE WATER TREATMENT

V. Vanitha<sup>1</sup>, N. Latha<sup>2\*</sup>

<sup>1</sup>Researcher scholar, Dept. of Chemistry, Kanadswami Kandar's College, P. Velur, Namakkal Tamilnadu.

<sup>2\*</sup>Asst. professor, Dept. of Chemistry, Department of Chemistry Kandaswami Kandar's College, Velur\*Tamil Nadu, India - 638182

\*Corresponding Author: - N. Latha

\*Email: [lathaankl@gmail.com](mailto:lathaankl@gmail.com)

## Abstract

Present study concentrated on the preparation of combined Mannich base with magnetic nano particle by condensation method. Various techniques were employed to confirm the formation of mannich base. The base is combined with magnetic nano particle and used to treat the phenolic effluent like o-cresol, 2-chlorophenol, 2, 6-dichlorophenol. Mannich base alone give 80.75% of removal after 4 days, when it mixed with magnetic Nanoparticle the result are remarkable it gives 94.14% removal in 1hr.

## Introduction

Mannich bases are known to possess potent activities like anti-inflammatory, anticancer, antifilarial, antibacterial, antifungal, anticonvulsant, anthelmintic, antitubercular, analgesic, anti-HIV, antimalarial, antipsychotic, antiviral activities. Along with biological activities these compounds are used in detergent additives, resins, polymers, surface active agents. The rich antimicrobial nature of mannich base it is used in waste water treatment to remove heavy metals. Mannich base like 1-(morpholino (phenyl) methyl) pyrrolidine-2, 5-dione, morpholine, succinimide, and Benzaldehyde, 1, 3-bis- (morpholin-4-yl-phenyl-methyl)-thiourea are already used to treat leather, paper and textiles, and the petroleum industry water treatment. And also used in analytical reagents, cosmetics, dye industries to remove heavy metals from effluents (Suman, T. et.al 2013)

Magnetic nano particles like Fe<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, and ferrotitanate are used in industries as coagulating agent to remove phenolic effluent, which can't be treat by normal coagulation and flocculation agents (Selvan et al., 20014.). Iron oxide nanoparticles are synthesized by three important methods such as physical, chemical, and biological. The main advantage of magnetic nanoparticles is that it produces a large amount of material, with control over particle size (2–20 nm) and shape afforded by adjusting pH, ionic strength, and the concentration of solution. Silica coated magnetic Nano adsorbents provide stability and increase adsorption efficiency (S. Sulochana et. al 2022). Silica-modified magnetite NPs functionalized with cetylpyridinium bromide complexation with 8-hydroxy quinoline used for detection of heavy metal ions such as Cd(II), Co(II), Cu(II), Mn(II), Ni(II), and Pb(II) from the water samples (Chakkaravarthi, K et.al 2014.). In this study instead of using silica we use mannich base as a combined material, which is already used as treating agent.

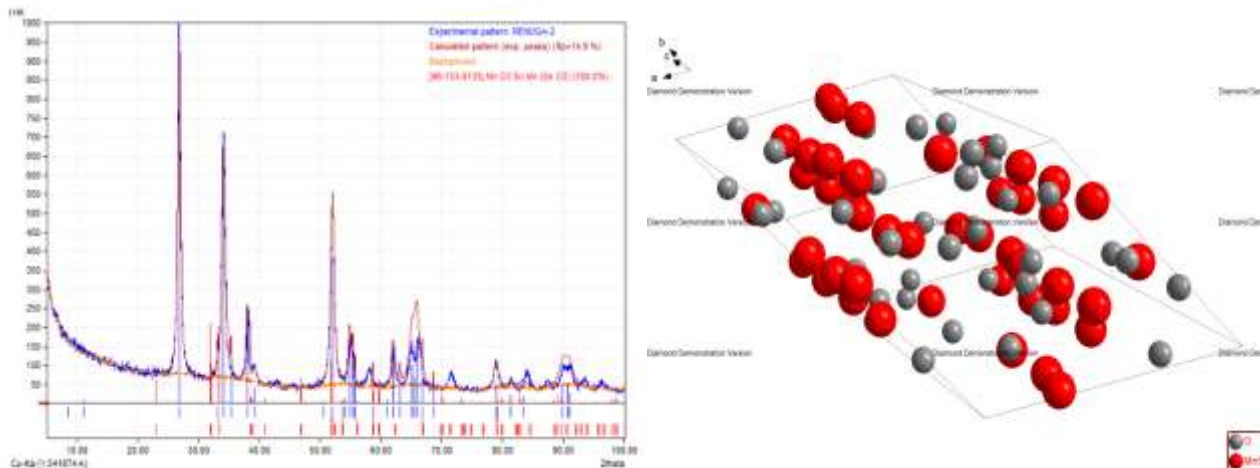
## Preparation of Pure Tin Oxide Nanoparticle

To prepare pure sample (1M) 11.28gm of tin chloride is dissolved in 50 ml of double distilled water stirred it about one and half hours, while stirring aqueous ammonia (3M) 15 ml added drop wise after one hour of completely add the ammonia solution the mixture become gel. After that the solution is heated to evaporate the water molecule then dry in hot air oven for about one hour in 80<sup>0</sup>C. Sample is calcinated in 400<sup>0</sup>C to obtained pure sample. Sample is stored for analysis and doping.

### Preparation of Mn Doped Material

Previously prepared Tin oxide sample is mixed with 0.1M,  $\text{MnSO}_4$  with polyethylene glycol (PEG 600). The same procedure is followed to dry and purify the sample.

### XRD

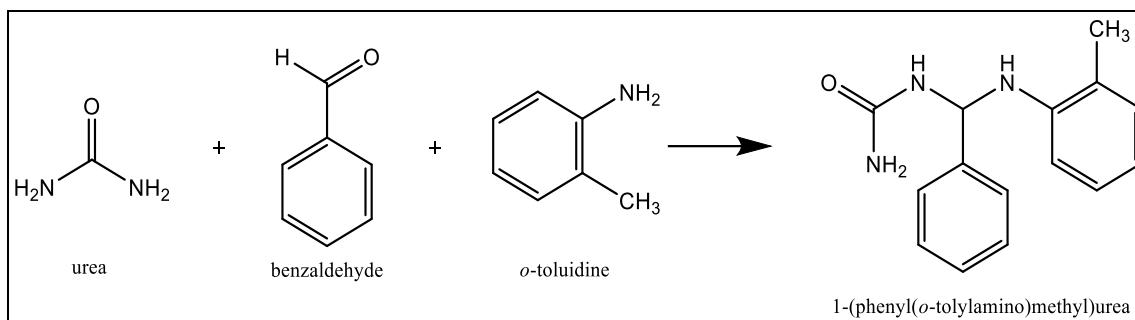


For doped sample it shows trigonal (rhombohedral axes) structure with R-3C space group for doped sample. The hkl values are changed due to doping this explained with the help of XRD as follows sample with 0.1M Mn doped shows high intensity peak d-value at 2.8005 Å (211) and 2.8720 Å (10-1). The change in hkl value shows doping exists in the sample (4). When the doping takes place the impurity added to the parent material due to the impurity the lattice arrangement of the parent material changed. When we add a known impurity to parent material the lattice disorder take place on it due to lattice disorder the morphology of the parent material was changed (R. Shanmuga Selvan, and K. Gokulakrishnan 2013).

### Synthesis procedure of 1-(phenyl(o-tolylamino)methyl)urea (OTUB)

1-(Phenyl(O-Tolylamino)Methyl)Urea (OTUB) synthesized by Mannich condensation reaction between 1,2,4-triazole, Succinimide and formaldehyde in 1:1:1 molar ratio. The O-Toluidine (1.07mL, 0.01N), Urea (0.67 gm, 0.01N) and Benzaldehyde (1.06mL, 0.01N) were taken in the equimolar ratio. A concentrated aqueous solution of Urea and O-Toluidine were prepared and mixed with constant stirring. Benzaldehyde was added in drops with continuous stirring of the reactant mixture. The mixture first became light creamy white in colour, then slowly turned into adull white crystalline mass and left it to complete the reaction. The product was separated by suction filtration and washed several times with acetone. The product was dried and recrystallized using chloroform by the slow evaporation method.

1-(phenyl (O-tolylamino) methyl) urea (OTUB) is a white colour solid, and it melted at 173-175°C. It is insoluble in water, but completely soluble in chloroform, Dimethyl formamide, and DMSO, etc., The percentage of the yield was 86.20%.



**Fig-1** formation of OTUB from reactant

### Structural Characterization of OTUB

The compound was analysed for carbon, hydrogen and nitrogen. The results of the theoretical elemental analysis of OTUB are given below.

### Elemental Analysis

**Table-1.** Theoretical Elemental Analysis of OTUB

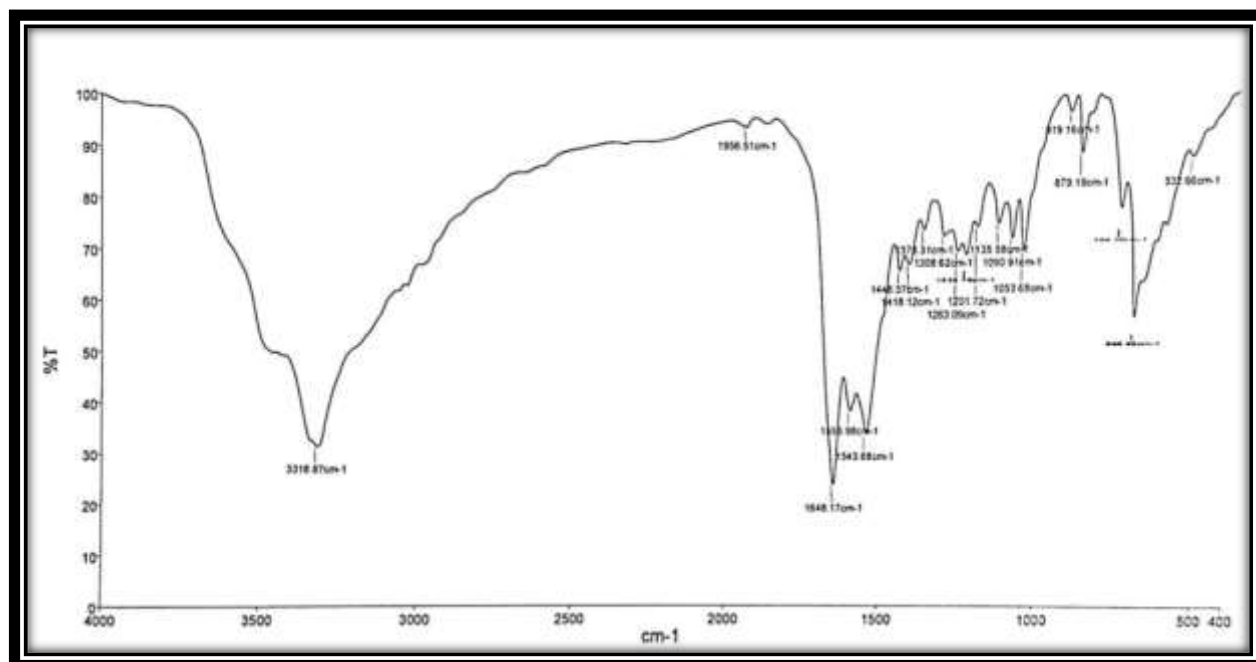
Elements	Calculated %
Carbon	70.56
Hydrogen	6.71
Nitrogen	16.46
Oxygen	6.27

The above Table-1 indicates the molecular formula of the compound as  $C_{15}H_{17}N_3O$  and the molecular weight is 255.14.

### Infrared spectral analysis (FTIR)

The infrared spectrum of OTUB was recorded on the KBr medium ( $4000-400\text{ cm}^{-1}$ ) as shown in Fig-2. The assignments of various stretching and bending frequencies for OTUB are listed in Table-2 and compared with those of Urea and O-Toluidine. The new absorption bands observed in the IR spectrum of OTUB show number of absorption bands, and the absorption frequencies are in a slightly shifted position in comparison with those of the reactants ( Selvan RS, Gokulakrishnan K. 2017).

This favourably indicates the substitution on O-Toluidine to diamide and formation of new compound. A sharp band observed at  $3318\text{ cm}^{-1}$  is assigned to  $\nu_{N-H}$  stretching vibration. The medium band at  $3065\text{ cm}^{-1}$  is attributed to aromatic and  $2923\text{ cm}^{-1}$  due to  $\nu_{C-H}$  aliphatic stretching vibration. The band in the region of  $1629$  and  $1585\text{ cm}^{-1}$  is due to  $\nu_{C=C}$  in ring stretching. The band at  $1648\text{ cm}^{-1}$  due to  $\nu_{C=O}$  stretching and the band at  $1543\text{ cm}^{-1}$   $\nu_{N-H}$  out of plane. The medium band at  $1201\text{ cm}^{-1}$  is due to the presence of  $\nu_{C-N-C}$  stretching vibration. The absorption band appears at  $1090\text{ cm}^{-1}$  in OTUB may be assigned to the stretching frequency of new  $\nu_{C-N-C}$  bond formed due to the formation of Mannich base. The presence of absorption bands in the region  $749-879\text{ cm}^{-1}$  is due to out of plane bending vibrations of  $\delta$  C-H bonds of aromatic ring.



**Fig-2** the FTIR Spectrum of OTUB

**Table-2** Important IR absorption bands ( $\text{cm}^{-1}$ ) of O-Toluidine, Urea and OTUB

O-Toluidine	Urea	OTUB	Tentative Assignment
3450	3447		
3367	3347	3318	
3219	3262	3318	VOH
-	-	-	VNH
3053	-	3065	$\nu_{\text{CH}}$ aromatic
3021	-	2923	$\nu_{\text{CH}}$ aliphatic
-	-	1956	$\nu_{\text{C}=\text{C}}$
-	-	1543	$\nu_{\text{C}=\text{N}}$
-	-	1448	$\nu_{\text{C}-\text{N}}$
-	-	1373	$\delta_{\text{CH}}$
-	-	1308	$\nu_{\text{CN}}$ , $\delta_{\text{CN}}$
-	-	1263,1201	$\nu_{\text{Ring}}$
-	-	1135	$\nu_{\text{C}-\text{N}-\text{C}}$
-	-	1090	$\nu_{\text{C}-\text{N}-\text{C}}$ Newly formed
-	-	1053	$\nu_{\text{C}-\text{C}}$ , $\delta_{\text{CH}_2}$ , $\delta_{\text{ring}}$
-	-	919	$\delta_{\text{CH}}$ i.p.b benzene
-	-	879	$\delta_{\text{CH}_2}$ o.o.p ring
-	-	749, 698, 532	$\delta_{\text{CH}}$ o.p.b benzene

The synthesized nano particles combined with mannich base and used to treat the non-biodegradable and toxic organic matters. The sample treatment was carried out using Jar test apparatus, and the sample was treated in different pH and time intervals to find the optimum pH. The magnetic nano particle was first used to treat the organic pollutant like chemicals O-Cresol, 2, 6-Chlorophenol, and 2-Dichlorophenol and the percentage of removal is observed using UV visible spectrum by the optical density method. For this study, we use  $\text{Al}_2\text{O}_3$  nanoparticle as a standard (Chakkaravarthi, K et. al 2013)

### Experimental procedure

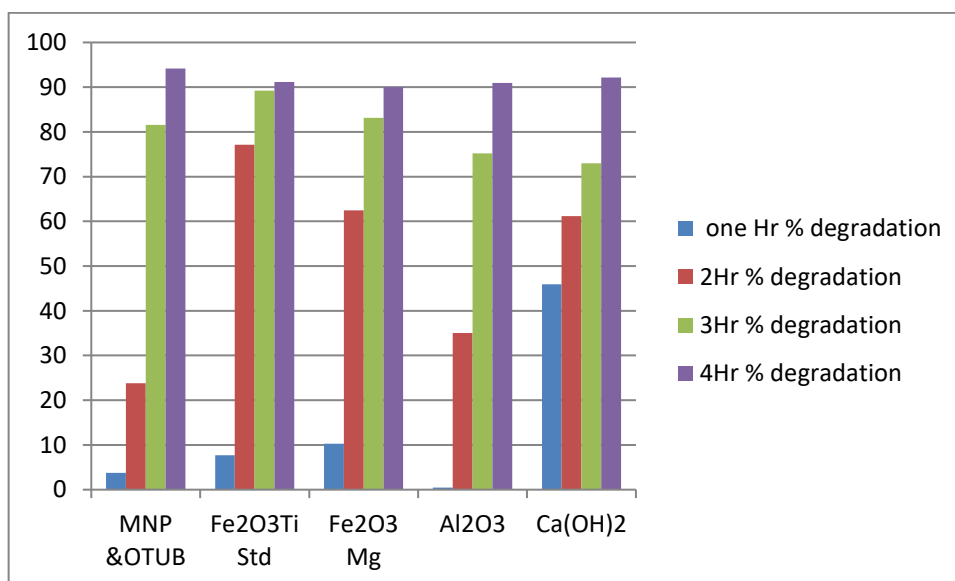
The test water treatment is made in 250 ml beaker; 100 ml of mixed phenolic effluent is taken in the beaker, 2 mg of magnetic nano particles added to it in room temperature. Beaker shaken well for equal distribution of magnetic nano particle. The external magnetic field is applied and the nano particle are immobilized 2 ml of the treated sample is taken into test tube and stock solution is added to it the color change takes place. The optical density is measured using UV spectrum. The procedure is repeated in various time intervals, Observations are listed in the table. Mixed wastes are collected and also used for test water treatment. Chemical o-cresol, were subjected to treat using mixed MNP and OTUB. Different concentrations were taken and compared with standard substrate (S. Philip Arockiaraj.et. al 2022)

### O-Cresol reduction experiments using mixed cultures

O-Cresol reduction experiment in wastewater was performed with five different initial concentrations (Ci) of cresol 50, 200, and 300 are common in industrial effluents and hence these concentrations were used. Some of the industrial effluents like petrochemical and coke oven effluents reports high concentration of o-cresols and for these reason studies were also performed for 500ppm of initial concentration. Compare the o-cresol degradation % for all using mixed MNP and standard. Following figures and charts shows the % degradation of o-cresol from 50ppm- 500ppm initial concentration. Also the pH changes indicate the removal of toxic compound from the reactor. O- Cresol was acetic in nature, and the wastewater is also acetic, but after the treatment pH changes to neutral (7.0-7.89) from acetic. Cell viability test also carried out after the complete degradation. It also shows positive results.

**Table O-** cresol degradation (mixed) for 50ppm

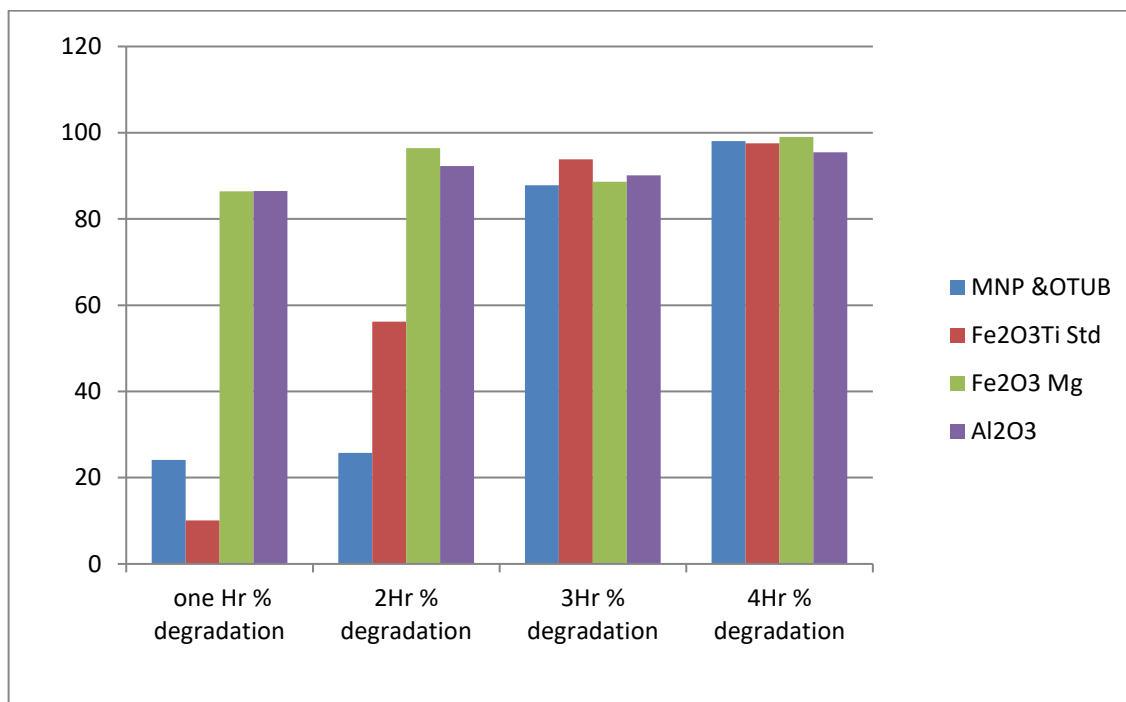
Name	1 Hr %	2Hr %	3Hr %	4Hr %
<b>MNP &amp;OTUB</b>	3.768	23.82	81.56	94.14
<b>Fe<sub>2</sub>O<sub>3</sub>Ti</b>	7.68	77.15	89.21	91.18
<b>Fe<sub>2</sub>O<sub>3</sub> Mg</b>	10.289	62.43	83.14	90.02
<b>Al<sub>2</sub>O<sub>3</sub></b>	0.434	35.07	75.21	90.95
<b>Ca(OH)<sub>2</sub></b>	45.945	61.15	72.95	92.17



**Fig:** 50ppm o-cresol removal by using mixed MNP

**Table O-cresol degradation (mixed) values for 200ppm**

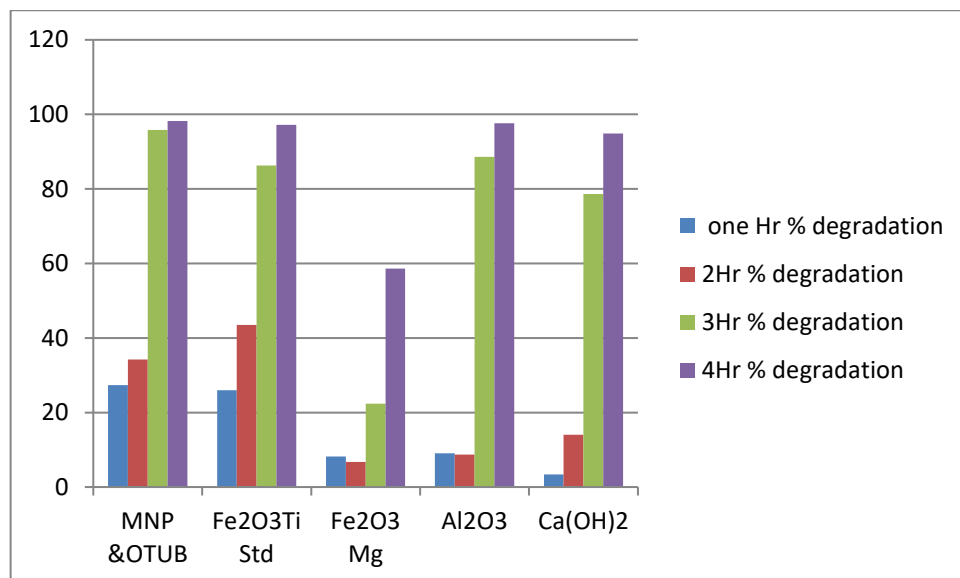
Reactor name	1 Hr %	2Hr %	3Hr %	4Hr %
<b>MNP &amp;OTUB</b>	24.13	25.76	87.82	98.04
<b>Fe<sub>2</sub>O<sub>3</sub>Ti Std</b>	10.07	56.19	93.84	97.53
<b>Fe<sub>2</sub>O<sub>3</sub> Mg</b>	86.44	96.41	88.62	99.05
<b>Al<sub>2</sub>O<sub>3</sub></b>	86.49	92.28	90.14	95.43
<b>Ca(OH)<sub>2</sub></b>	17.24	94.23	92.75	97.6



**Fig-200ppm o-cresol removal using mixed MNP**

**Table-O-Cresol degradation (mixed) values for 300ppm**

Reactor name	1Hr	2Hr %	3Hr %	4Hr %
<b>MNP &amp;OTUB</b>	27.34	34.2	95.85	98.18
<b>Fe<sub>2</sub>O<sub>3</sub>Ti Std</b>	25.99	43.47	86.24	97.17
<b>Fe<sub>2</sub>O<sub>3</sub> Mg</b>	8.21	6.763	22.41	58.62
<b>Al<sub>2</sub>O<sub>3</sub></b>	9.08	8.691	88.56	97.63
<b>Ca(OH)<sub>2</sub></b>	3.38	14.02	78.59	94.9



**Fig-** 300ppm O-Cresol removal using mixed culture

## CONCLUSION

The prepared OTUB and MNP were characterized by various instruments and confirmed their properties. From X-ray the prepared tin nano particle has R-3C and purity of sample was confirmed. The structure and composition of OTUB were confirmed with IR and elemental study.

In this study researcher tested potential treatment for wastewater containing o-cresol, and mixed effluent using mixed MNP & OTUB some other commonly available flocculating agent. The results show the high potential applications in wastewater remediation. More than 90% of o-cresol removal was observed. Even for higher concentration (500ppm) of o-cresol.

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