Retarding of Preliminary Chemical Pollutants from Dye Industry Effluents by Metal Nano Particles, Synthesized Using Flower Extract of *Catharanthus roseus*

VIJAYA ANANDAN VEERASAMY ALAGARSAMY[1], KISTAN ANDIYAPPAN[1,2]*
SARAL ABDUL KADAR AVULIYA[2] and THAMINUM ANSARI ABUBACKER[3]

[1]Research and Development Centre, Bharathiar University, Coimbatore- 641046, Tamil Nadu, India
[2]Panimalar Institute of technology, Chennai, India.
[3]PG & Research Department of Chemistry, Muthurangam Government Arts College,
Vellore 632002, Tamil Nadu, India.
*Corresponding author E-mail: vishmikrish@gmail.com

ABSTRACT

The present research discussed usage of 3 inorganic nano-substances in order to retard chemical pollutants from coloured effluents of dye industry and tanneries. These 3 inorganic Nano metal particles synthesized from $MgSO_4$, $CuSO_4.5H_2O$ and $FeSO_4.75H_2O$ with rose petals extract *Catharanthus roseus*. To assess the feasibility of using these nano particles as low-cost adsorbents for suppressing preliminary chemical pollutants in coloured effluents. Also compared and investigated the ability of these 3 nano materials due to using flower extract of *Catharanthus roseus* petals, in order to retard preliminary chemical pollutants quantity such as pH, Alkalinity, hardness, TDS, BOD, COD, Sulphide, Sulphate, Nitrate, Ca, Mg, Phosphate, Na and K. These synthesized 3 nano materials characterized by UV-Visible spectroscopic analysis, FT-IR Spectroscopic analysis and, X-ray Diffraction (XRD) studies.

Keywords: Nano materials, *Catharanthus roseus*, Low cost adsorbent, Preliminary pollutants, Dye effluents.

INTRODUCTION

Now a day we know numerous management approaches to remove contaminants from dye industry and tannery sewage. This removal process can be carried out by physical, chemical, and biological processes[1]. In the chemical management procedure, many advanced process such as UV, H_2O_2, photo-catalyst and Fenton's agent are often used and have been proven effective in the quick elimination of colours and pollutants from dye solutions[2]. Over the previous few years adsorption

has gained paramount importance in industry and surroundings protection. Adsorbents are generally used for its environment pleasant conduct, availability in nature and are very a good deal-price powerful. Metal Nano particles can be used as effective bio-adsorbent for removing with dyes metals and natural pollutants from industrial wastewater.

However those technologies usually having some disadvantages, such as complicated procedure, high expenses, forming by-products and removal of those by-products. For example activated carbon is typically extra effective to adsorb numerous pollutants than other adsorbents which do now not require massive processing[3]. But, commercially available activated carbon is highly-priced and might not be cost effective for colored wastewater remedy. For a cost-effective colored wastewater remedy purpose, therefore the improvement of recent materials from no price or low cost adsorbents obtained domestically is a thrilling alternative. Many research had been investigated the remedy of dye effluents containing a single dye or a aggregate of the identical magnificence of dyes, as well as chemical contaminants however the treatment of mixtures containing distinct lessons of dyes has not been sufficiently addressed[4]. The present look at investigates the effectiveness of adsorption as a treatment manner for a disperse dye, a reactive dye and their aqueous mixtures, in phrases of retardation of chemical parameters consisting of pH, alkalinity, hardness, TDS, BOD, COD reduction the usage of inorganic synthesized nano materials ($MgSO_4$, $CuSO_4 5H_2O$, $FeSO_4.7H_2o$).

Novelty of present study was some inorganic metal Nanoparticles are synthesized by using the flower extract of the plant *Catharanthus roseus* (also known as periwinkle) belongs to the family Apocyanaceae; it grows as a shrub in subtropical areas. The plant produces flowers with five petals and the flowers are of three types. Rose purple flowers, white flowers and white flowers with a rose purple spot in the centre. The first type is most commonly found and it is more cultivated because of its higher alkaloid content. This plant has been taken for study due to its unique properties. This examine was achieved to make use of the steel

Nano particles as a low value adsorbent with recognize to numerous parameters together with exclusive doses, contact time and pH. The characterizations of these Nanoparticles were done by FTIR, UV-spectroscopy, and XRD analysis.

MATERIALS AND METHODS

Preparation of rose extracts
Materials used for the synthesis of Nano particles are $MgSO_4$, $CuSO_4.5H_2O$, $FeSO_4.7H_2O$, were purchased from Merck–chemical company, India. The flowers of the plant *Catharanthus roseus* were collected from rose garden. 10 g wet flowers petals were weighed and washed twice with distilled water followed by Millipore water and then macerated into fine pieces. These fine flower petal pieces taken in a 250 ml Erlenmeyer flask, 50 ml of Millipore water was added and kept on a water bath for 15 min. at 750 °C. Then the flowers content was filtered off through whatman 40 clear out paper after which extract become used for the synthesis of diverse metals nano debris which includes $MgSO_4$, $CuSO_4.5H_2O$, and $FeSO_4.7H_2O$. This extract stands stable for one week if stored at 30±5 °C.

Synthesis of Metal Nano particles using Rose petal extract
Synthesis of $MgSO_4$ Nano particle
200 ml of the solution of $MgSO_4$ (4.92 g) and then stirred by magnetic stirring (1000 Rpm) for 60 min. and then this mixture was added slowly with constant agitation in the titrant of 200 ml of NaOH (0.1N) solution then precipitate was obtained. This precipitate was filtered and dried at the oven 150 °C. The precipitate obtained in this process was characterized by UV-Visible spectroscopic analysis, FT-IR Spectroscopic analysis, X-ray diffraction studies.

Synthesis of $CuSO_4.5H_2O$ Nano particle
200 ml of the solution of $CuSO_4.5H_2O$ (4.99 g) and then stirred by magnetic stirring (1000Rpm) for 60 min. and then this mixture was added slowly with constant agitation in the titrant of 200ml of NaOH (0.1N) solution then precipitate was obtained. This precipitate was filtered and dried at the oven 150 °C. The precipitate obtained in this process was characterized by UV-Visible spectroscopic analysis, FT-IR Spectroscopic analysis, X-ray Diffraction Studies.

Synthesis of $FeSO_4.7H_2O$ Nano particle

200 ml of the solution of $FeSO_4.7H_2O$ (5.56 g) and then stirred by magnetic stirring (1000 Rpm) for 60 min. and then this mixture was added slowly with constant agitation in the titrant of 200 ml of NaOH (0.1N) solution then precipitate was obtained. This precipitate was filtered and dried at the oven 150 °C. The precipitate obtained in this process was characterized by UV-Visible spectroscopic analysis, FT-IR Spectroscopic analysis, X-ray diffraction studies.

Characterization of metal nano particles
UV-Visible spectroscopic analysis

UV-Visible spectra of all the nanoparticle were recorded using de-ionized water (H_2O) as solvent[6]. The UV-Visible spectra of Rose extract and metal nanoparticle are given in Fig. 1-3, and the values are shown in Table. 1.The spectrum reveals the characteristic absorption peaks of Nanoparticle material at 200-590 nm respectively. The maximum peak was observed at 380 nm and minimum peak was observed at 230 nm which corresponds to Nano size of $MgSO_4$. The maximum peak was observed at 590 nm and minimum peak was observed at 390nm which corresponds to Nano size of $CuSO_4.5H_2O$. The maximum peak was observed at 393 nm and minimum peak was observed at 242 nm which corresponds to nano

Table. 1: UV-Visible spectral data of different metal nano particle

Types of Nano materials	λ_{max} (nm)
$MgSO_4$	235 & 380
$CuSO_4.5H_2O$	390 & 590
$FeSO_4.7H_2O$	242 & 393

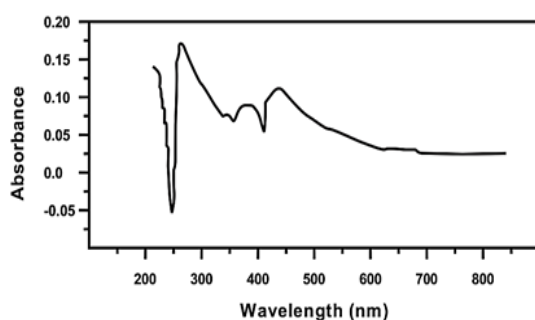**Fig. 1. UV-Spectral Analysis of $MgSO_4$ Nanoparticl**

size of $FeSO_4.7H_2O$. UV-Visible Spectra revealed that concentration of aqueous extract of Catharanthus roseus plays an important role in the charge transfer from oxygen to the center; one can expect to see the metal field transition in these cases.
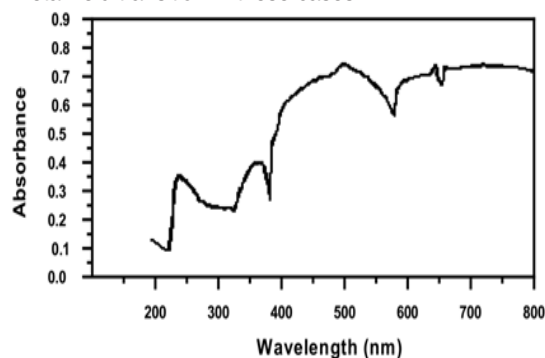

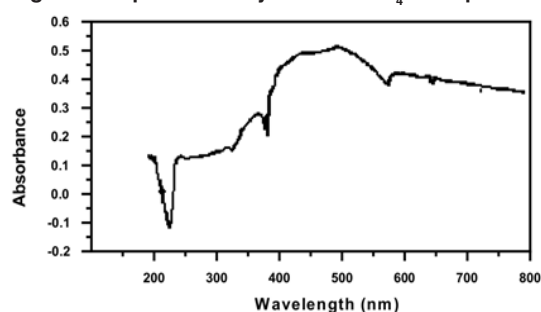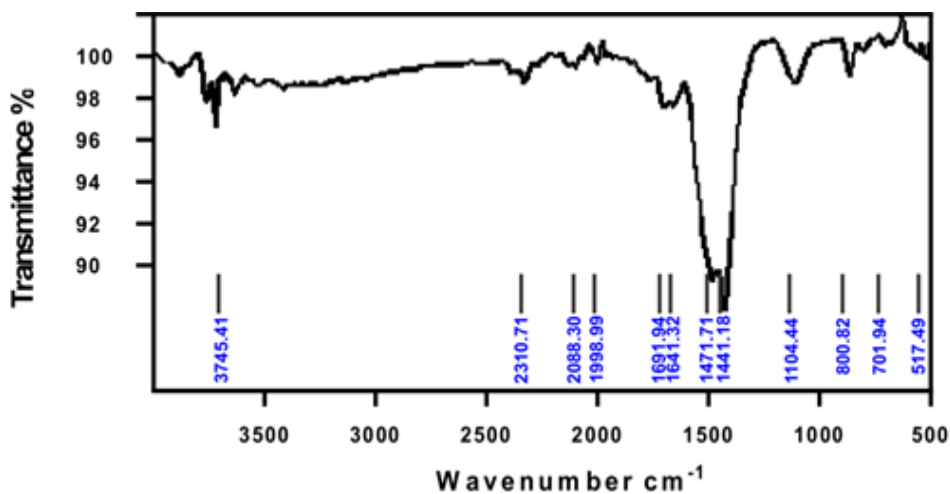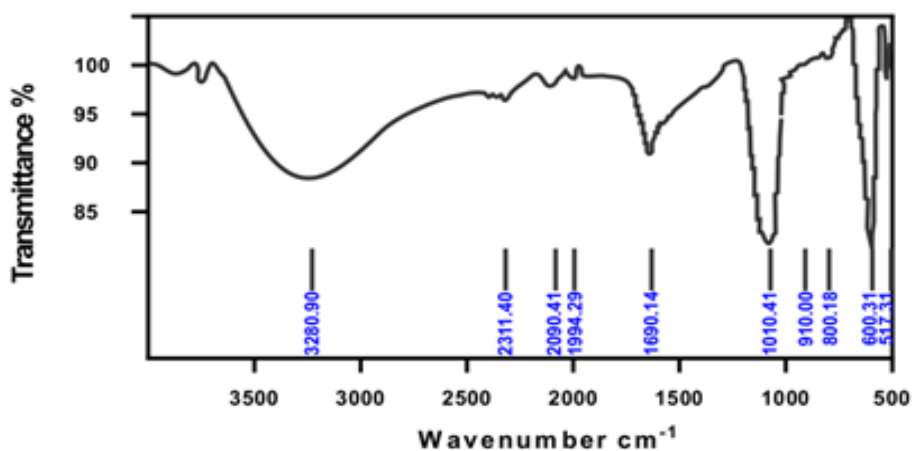**Fig. 2. UV-Spectral Analysis of $CuSO_4$ Nanoparticle**

Fig. 3. UV -Spectral Analysis of $FeSO_4.7H_2O$ Nanoparticle

FT-IR Spectroscopic analysis

FT-IR spectrum of the metal nano particles shows peak at 500 cm^{-1} to 650 cm^{-1} which is attributed to the presence of metal in the nanoparticle. The band at 3850.22 cm^{-1} - 1481.48 cm^{-1}, 1078.41 cm^{-1} - 899.21 cm^{-1} and 3682.12 cm^{-1} 988.88 cm^{-1} are attributed to $MgSO_4$, $CuSO_4.5H_2O$ and $FeSO_4.7H_2O$ stretching mode of vibration for the benzenoid units of rose extract. The FT-IR spectroscopic analysis of rose extract and metal

Table. 2: IR-Vibration Frequencies for the Rose Extract and Metal Nanoparticle

Types of Nano materials	Wave number (cm^{-1})
MgSO4	3850.22 & 1481.48
$CuSO_4.5H_2O$	1078.41 & 899.21
$FeSO_4.7H_2O$	3682.12 & 988.88

Fig. 4. IR-Spectral Analysis of MgSO$_4$ Nanoparticle
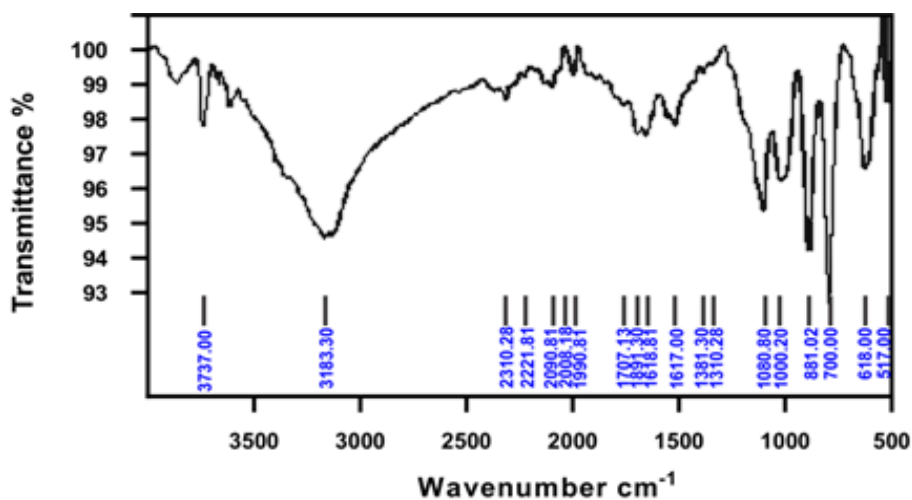

Fig. 5. IR-Spectral Analysis of CuSO$_4$ Nanoparticle

Fig. 6. IR-Spectral Analysis of FeSO$_4$.7H$_2$O Nanoparticle

Nanoparticle are given in Fig. 4-6, and the values are shown in Table. 2.

X-ray Diffraction Studies

Figure. 7 -9 shows the XRD pattern of $MgSO_4$, $CuSO_4.5H_2O$ and $FeSO_4.7H_2O$ nanoparticles. XRD diffraction patterns of $MgSO_4$, $CuSO_4.5H_2O$ and $FeSO_4.7H_2O$ nanoparticles. On comparison with the JCPDS data's (21-1272, 04-0836, 85-1436, 89-1397,04-0836) reveals that the crystalline structure of nanoparticles which are Hexagonal, Cubic, Spinel Cubic, Structure[7]. Average particle diameter D for specimen was obtained from the main peak using Debye-Scherrer equation (1) for

the peak width broadening as a function of the size of the particles.

$$D=0.89 / \beta cos\theta \rightarrow \qquad (1)$$

Here λ is the x-ray wavelength ($K\alpha$=1.5418a°),k is the system constant(0.89), β is the total width at half most of the peak and θ is the peak function and using the above method we obtained a median length for debris with the greater intense height of the plane for sample[8]. The average size of the nanoparticles was shown in Table. 3. XRD study clearly confirms that the formation of rose extract dispersed in nanoparticles which are, $MgSO_4$, $CuSO_4.5H_2O$ and $FeSO_4.7H_2O$.
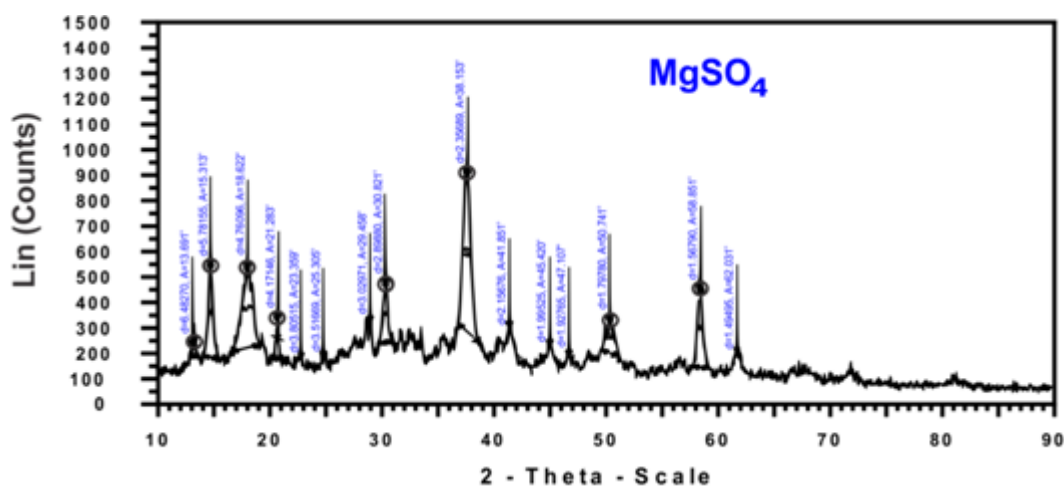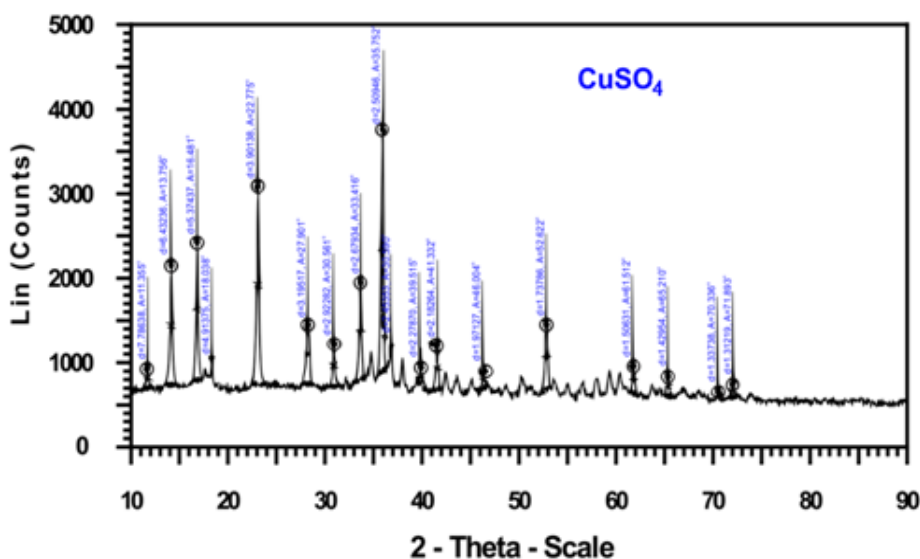

Figure: 7 XRD-Spectral Analysis of MgSO₄ Nanoparticle

Fig.8.XRD-Spectral Analysis of CuSO₄ Nanoparticle
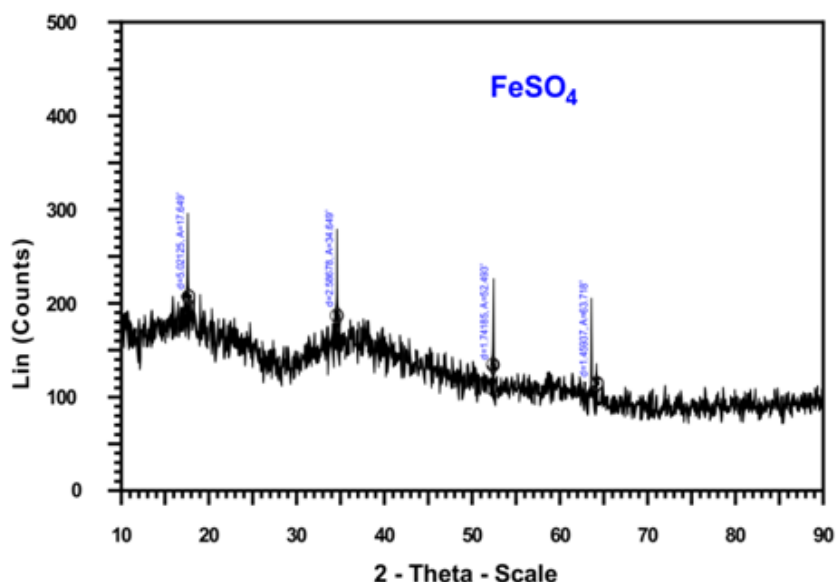
Fig. 9. XRD-Spectral Analysis of $FeSO_4.7H_2O$ Nanoparticle

Table.3: X-ray Diffraction Studies for the Rose Extract and Metal Nanoparticles

Types of XRD Nanoparticles Compund	Average Crystalline Size (D)nm	$2(\theta)$
$MgSO_4$	7.220	18.622
$CuSO_4.5H_2O$	35.019	18.038
$FeSO_4.7H_2O$	29.98	63.718

Methodology
Analytical analysis

      The Physico-chemical parameters such as pH, TDS, BOD, COD, Total alkalinity, Potassium, Calcium, Magnesium, Sulphides, Chlorides, Chromium and Nitrates were determined, the chemical characteristics including heavy metals for examination of water[10].

      The physico-chemical parameters such as pH, TDS, BOD, COD, overall Alkalinity, Potassium, Calcium, Magnesium, Sulphides, Chlorides, Chromium and Nitrate have been measured on the sample web page the usage of hand held analyzing kits. Ground water samples have been amassed and the samples were saved in a polythene bottle for similarly laboratory analysis of fundamental ions. The extra natural analytical reagents and chemical requirements had been used for the groundwater excellent assessment. The water samples were analyzed in Tamilnadu Water Supply and Drainage Board, Vellore.4.

      The analytical techniques are suggested by the American Public Fitness Association[11]. pH was determined by electrometric method by using pH meter. (Alkalinity) Carbonate and bicarbonate were determined using acid - base titration method; Total alkalinity was measured by potentiometric titration method. TDS was determined by Gravimetric method. Chloride concentration was measured by Argentometric method, Sulphate and sulphide measured by Colorimetric method using spectrophotometer, Nitrate was analyzed using Kjeldhal flask apparatus. Calcium and Magnesium were determined using the EDTA titration method Chromium were determined by Flame Atomic Absorption Spectrophotometer (VARIAN SPECTRA A240) in CVR Labs Pvt. Ltd, Saidapet, Chennai-5, Tamilnadu.

Pretreatment with metal nano particles

      Waste water samples from equalization cum collection tank were taken in four 1 litre graduated glass jars. To each of the sample with three metal nano particles namely $MgSO_4$, $CuSO_4.5H_2O$, and $FeSO_4.7H_2O$ at various concentrations (10 mg/lit., 20 mg/lit., 30 mg/lit., and 40 mg/lit, 50mg/lit.) were added and allowed to settle

for 12 hours. The supernatant liquid was used for the tests of various parameters such as pH, COD, BOD, chlorides, Sulphide, hardness, alkalinity, Nitrate and TDS by quantitative methods.

RESULT AND DISCUSSION

The waste water samples from equalization cum collection tanks of selected dye industries were collected and characterized for pH, COD, BOD, SS and TDS, the data are presented in Table . 4.

Table.4: Characterization of raw sample

S.NO	Parameters	Unit	Before adding adsorbents
1.	pH at 25°C	Number	8.5
2.	Total Dissolved solids at 180°C	Mg/L	15,216
3.	Chlorides as Cl	Mg/L	3500
4.	Sulphide as SO_4	Mg/L	1900
5.	BOD (at 27°C for 3 days)	Mg/L	600
6.	COD	Mg/L	3400
7.	Alkalinity	Mg/L	7000
8.	Total hardness	Mg/L	4500
9.	Calcium	Mg/L	3000
10.	Magnesium	Mg/L	900
11.	Sulphide	Mg/L	27
12.	Phosphate	Mg/L	1.59
13.	Sodium	Mg/L	800
14.	Potassium	Mg/L	30
15.	Nitrate	Mg/L	5.10

The BOD/COD ratio can likely to be increased remaining certain residual non-biodegradable organic materials and chemicals in the dye waste water. The settling rate of sludge appeared from primary liquor was observed to be 0.024. Actually the BOD/COD ratio which is an index of waste water was found to be in the range of 0.15 to 0.35. The settling rate of sludge is a function of particle size and viscosity of the medium. The size of the particles can be increased during adsorption and flocculation due to the addition of adsorbents.

Chemical adsorption consists of adding small amount of certain adsorbent to waste water which form flocculation precipitate that coalesce the suspended impurities can cause force to settle out rapidly. Adsorbent consists of a series of operation that result in the destabilization of the colloids leading to their removal from the suspended fluid. Ideally it is possible to distinguish from sequential steps in adsorption namely.

- v Dispersion of adsorbent
- Nucleation
- Flocculation and
- Phase separation

In current practice, PACL is used as the best adsorbent for dye waste water. The quantity of adsorbent PACL required for adsorption-flocculation of waste water was optimized for the removal of suspended solid and other organics in it. The results that were obtained for optimum dosage of alum as coagulant was already studied.

PACL is the best adsorbent for dye effluent. The quantity of the adsorbent was optimized in the preliminary investigations Table. 2. In the acidic location, PACL starts to hydrolyze and paperwork monomeric al hydrolyzed species. Subsequently, soluble cations such as Al^{3+}, Al $(OH)^{2+}$ and Al $(OH)^{2+}$ are most important within the answer. They play an important role in destabilizing the negatively charged dye debris via fee neutralization. At around impartial pH, Al(III) has constrained solubility because of the precipitation of amorphous hydroxide, which results in the possibility of sweep flocculation as impurities (i.e., dye particles) enmesh inside the developing precipitates and are efficaciously removed. The main purpose of this study is the new adsorbents namely $MgSO_4$, $CuSO_4.5H_2O$, $FeSO_4.7H_2O$ and were introduced and tried for the first time, as adsorbent for textile industry dye effluent to know their removal efficiencies in controlling various pollution causing parameters of dye effluents and their effectiveness were compared with that of Pearl Agrotech Corporation Limited (PACL).

The values presented in the tables were the results obtained for samples with different nano materials in various concentrations. And also the

graphs were plotted for reduction of physico chemical pollutants against dosages of synthesized nano materials Adsorbent.

The present study further extended to employ new adsorbents, metal nano particles synthesized using rose petals (catharanthus roseus) such as $MgSO_4, CuSO_4.5H_2O$ and $FeSO_4.7H_2O$ to compare the results with those obtained with PACL. Data obtained for the different complexes are presented in Tables. 5, 9.

Effect of MgSO$_4$ nano particles on vat dye combined waste water

The pH of the raw effluent was 8.5 it was decreases to 8.5, 8.6, 8.8, 8.9, and 9.4 with addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of $MgSO_4$ nano particles respectively Table. 5 due to the basic nature of the coagulant. The increase of pH might due to the release of the hydroxide ions in the complexes depict the change of pH as a function of the coagulant concentration.

The Total Dissolved Solid value of the raw effluent was 15,216 mg/L and decrease to 6520 mg/L , 6490 mg/L , 6471 mg/L , 6432 mg/L and 6330 mg/L with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit,50 mg/lit of $CuSO_4.5H_2O$ nano particles respectively Table. 5. It was observed that there was reduction of TDS was imparted by the $MgSO_4$ nano particles added. The main objective of chemical treatment is to remove colloids carried by the effluent. Since colloidal particles are charged particles, and these charged particle trapped using complexes carrying opposite charges in order to form flock and create density gradient between liquid and suspended solid phase (to reduce zeta potential of suspended colloidal particles).

The chloride value of the raw effluent was 3500 mg/lit. It was decreases to 1194 mg/lit, 1183 mg/lit, 1143 mg/lit., 1168 mg/lit, and 1127 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, and 50 mg/lit. of $MgSO_4$ nano particles respectively Table. 5. The reduction in the chloride value might be due to the replacement of chloride by perchlorate ions in plain sedimentation.

The sulphate value of the raw effluent was 1900 mg/lit. It was decreases to1397 mg/lit, 1351 mg/lit, 1297 mg/lit, 1275 mg/lit and 1243 mg/lit. with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit,50 mg/lit of $MgSO_4$ nano particles respectively Table. 5. The reduction in the Sulphate value might be due to the oxidation of Sulphate form into elementary sulphur, which formed flocculation and undergo plain sedimentation**.**

The BOD of the raw effluent was 350 mg/lit and decreases to 324 mg/lit, 312 mg/lit , 298 mg/lit, 286 mg/lit, and 273 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit,50 mg/lit of $MgSO_4$ nano particles respectively Table. 5. The decrease in BOD might be due to coagulating effect of the complex with bio-organic compounds. It is evident that heavy metals are toxic to aquatic microorganisms beyond certain concentration.

The COD value of the raw effluent was 2311 mg/lit and decrease to 2198 mg/lit, 2143 mg/lit, 2083 mg/lit, 2041 mg/lit, and 2005 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit,50 mg/lit of $MgSO_4$ nano particles respectively Table. 5. This reduction in COD might be due to nitrogenous increment in waste water by addition of dosed $MgSO_4$ nano particles.

The Alkalinity of the raw effluent was 2860 mg/lit and decrease to 2630 mg/lit, 2542 mg/lit, 2367 mg/lit, 2277 mg/lit, and 2168 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit,50 mg/lit of $MgSO_4$ nano particles respectively Table. 5.

The total hardness of the raw effluent was 2000 mg/lit and decrease to 1414 mg/lit, 1383 mg/lit, 1375 mg/lit, 1366 mg/lit, and 1361 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of $MgSO_4$ nano particles respectively Table. 5.

The calcium value of the raw effluent was 1080 mg/lit and decrease to 926 mg/lit, 904 mg/lit, 891 mg/lit, 876 mg/lit, and 863 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of $MgSO_4$ nano particles respectively Table. 5.

The magnesium value of the raw effluent was 520 mg/lit and decrease to 462 mg/lit, 448 mg/lit, 422 mg/lit, 409 mg/lit, and 399 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of $MgSO_4$ nano particles respectively Table. 5.

The phosphate value of the raw effluent was 0.28 mg/lit and decrease to 0.22 mg/lit, 0.20 mg/lit, 0.17 mg/lit, 0.15 mg/lit, and 0.13 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of $MgSO_4$ nano particles respectively Table. 5.

The sodium value of the raw effluent was 490 mg/lit and decrease to 473 mg/lit, 471 mg/lit, 467 mg/lit, 463 mg/lit, and 458 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of $MgSO_4$ nano particles respectively Table. 5.

The potassium value of the raw effluent was 17 mg/lit and decrease to 13 mg/lit, 12 mg/lit, 11 mg/lit, 9 mg/lit, and 7 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of $MgSO_4$ nano particles respectively Table. 5.

The nitrate value of the raw effluent was 2.00 mg/lit and decrease to 1.90 mg/lit, 1.85 mg/lit, 1.81 mg/lit, 1.77 mg/lit, and 1.74 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of $MgSO_4$ nano particles respectively Table. 5.

Effect of $CuSO_4.5H_2O$ nano particles on dye combined waste water

The pH of the raw effluent was 10.2 It was decreases to 9.7, 9.5, 9.4, 9.2 and 8.9 with addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of $CuSO_4.5H_2O$ nano particles respectively Table.6 due to the basic nature of the coagulant. The increase of pH might due to the release of the hydroxide ions in the complexes depict the change of pH as a function of the coagulant concentration.

The total dissolved solid value of the raw effluent was 14,692 mg/lit and decrease to 12,300 mg/lit , 12,000 mg/lit ,11,700 , 11,100 mg/lit and 10,400 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit,50 mg/lit of $CuSO_4.5H_2O$ nano particles respectively Table-6. It was observed that there was reduction of TDS was imparted by the $CuSO_4.5H_2O$ nano particles added. The main objective of chemical treatment is to remove colloids carried by the effluent. Since colloidal particles are charged particles, and these charged particle trapped using complexes carrying opposite

Table. 5:   Characterization of Dye effluent with $MgSO_4$ nano particle

S.NO	Parameters	Unit	Raw Sample	10 Mg/L	20 Mg/L	30 Mg/L	40 Mg/L	50 Mg/L
1.	pH at 25 °C	Number	8.5	8.6	8.8	8.8	8.9	9.4
2.	Total Dissolved solids at 180°C	Mg/L	15,216	8520	6490	6471	6432	6330
3.	Chlorides as Cl	Mg/L	3500	1194	1183	1143	1168	1127
4.	Sulphide as SO_4^{2-}	Mg/L	1900	1397	1351	1297	1275	1243
5.	BOD (at 27 °C for 3 days)	Mg/L	600	324	312	298	286	273
6.	COD	Mg/L	3400	2198	2143	2083	2041	2005
7.	Alkalinity	Mg/L	7000	2630	2542	2367	2277	2168
8.	Total hardness	Mg/L	4500	1414	1383	1375	1366	1361
9.	Calcium	Mg/L	3000	926	904	891	876	863
10.	Magnesium	Mg/L	900	462	448	422	409	399
11.	Sulphide	Mg/L	27	11	8	6	5	3
12.	Phosphate	Mg/L	1.59	0.22	0.20	0.17	0.15	0.13
13.	Sodium	Mg/L	800	473	471	467	463	458
14.	Potassium	Mg/L	30	13	12	11	9	7
15.	Nitrate	Mg/L	5.10	1.90	1.85	1.81	1.77	1.74

charges in order to form flock and create density gradient between liquid and suspended solid phase (to reduce zeta potential of suspended colloidal particles).

Chloride value of the raw effluent was 2680 mg/lit. It was decreases to 2400 mg/lit, 2325 mg/lit, 2240 mg/lit., 2180 mg/lit, and 2100 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, and 50 mg/lit of $CuSO_4.5H_2O$ nano particles respectively Table. 6. The reduction in the chloride value might be due to the replacement of chloride by per chlorate ions in plain sedimentation.

Sulphate value of the raw effluent was 4418 mg/lit. It was decreases to 4239 mg/lit, 4180 mg/lit,3972 mg/lit,3680 mg/lit and 3379 mg/lit. with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit,50 mg/lit of $CuSO_4.5H_2O$ nano particles respectively Table. 6. The reduction in the Sulphate value might be due to the oxidation of Sulphate form into elementary Sulphur, which formed flocculation and undergo plain sedimentation.

The BOD of the raw effluent was 486 mg/lit and decreases to 430 mg/lit, 425 mg/lit , 415 mg/lit, 405 mg/lit, and 400 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit,50 mg/lit of $CuSO_4.5H_2O$ nano particles respectively Table. 6. The decrease in BOD might be due to coagulating effect of the complex with bio organic compounds. It is evident that heavy metals are toxic to aquatic microorganisms beyond certain concentration.

The COD value of the raw effluent was 3560 mg/lit and decrease to 3200 mg/lit, 3120 mg/lit, 3040 mg/lit, 2970 mg/lit, and 2880 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit,50 mg/lit of $CuSO_4.5H_2O$ nano particles respectively Table. 6. This reduction in COD might be due to nitrogenous increment in waste water by addition of dosed complexes.

The Alkalinity of the raw effluent was 6900 mg/lit and decrease to 6200 mg/lit, 6175 mg/lit, 6150 mg/lit, 6120 mg/lit, and 6100 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit,50 mg/lit of $CuSO_4.5H_2O$nano particles respectively Table. 6.

The total hardness of the raw effluent was 7000 mg/lit and decrease to 6500 mg/lit, 6460 mg/lit, 6400 mg/lit, 6340 mg/lit, and 6300 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of $CuSO_4.5H_2O$ nano particles respectively Table. 6.

Calcium value of the raw effluent was 2100 mg/lit and decrease to 1400 mg/lit, 1384 mg/lit, 1372 mg/lit, 1367 mg/lit, and 1362 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of $CuSO_4.5H_2O$nano particles respectively Table. 6.

The Magnesium value of the raw effluent was 840 mg/lit and decrease to 729 mg/lit, 717 mg/lit, 702 mg/lit, 693 mg/lit, and 680 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of $CuSO_4.5H_2O$nano particles respectively Table. 6.

Sulphide value of the raw effluent was 18 mg/lit and decrease to 12 mg/lit, 11 mg/lit, 10 mg/lit, 9 mg/lit, and 8 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of $CuSO_4.5H_2$On ano particles respectivelyTable. 6.

Phosphate value of the raw effluent was 0.78 mg/lit and decrease to 0.62 mg/lit, 0.58 mg/lit, 0.47 mg/lit, 0.35 mg/lit, and 0.33 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of $CuSO_4.5H_2O$nano particles respectively Table. 6.

Sodium value of the raw effluent was 980 mg/lit and decrease to 900 mg/lit, 885 mg/lit, 872 mg/lit, 861 mg/lit, and 840 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of $CuSO_4.5H_2O$nano particles respectively Table. 6.

Potassium value of the raw effluent was 32 mg/lit and decrease to 25 mg/lit, 17 mg/lit, 14 mg/lit, 13 mg/lit, and 11 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of $CuSO_4.5H_2O$nano particles respectively Table. 6.

Nitrate value of the raw effluent was 3.03 mg/lit and decrease to 2.37 mg/lit, 2.12 mg/lit, 1.82 mg/lit, 1.74 mg/lit, and 1.60 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of $CuSO_4.5H_2O$ nano particles respectively Table. 6.

The pH of the raw effluent was 8.5. It was increased to 8.5, 8.8, 9.0, 9.2, and 9.8 with addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of nano adsorbent of $FeSO_4.7H_2O$ respectively Table. 7 due to the basic nature of the coagulant. The increase of pH might due to the release of the hydroxide ions in the complexes depict the change of pH as a function of the coagulant concentration.

The total dissolved solid value of the raw effluent was 15,216 and decrease to 13,172mg/l , 13,041 mg/l ,12,840 mg/l , 12,520 mg/l and 12,163 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of nano adsorbent of $FeSO_4.7H_2O$ respectively Table. 7. It was observed that there was reduction of TDS was imparted by the chemicals added. The main objective of chemical treatment is to remove colloids carried by the effluent. Since colloidal particles are charged particles, and these charged particle trapped using complexes carrying opposite charges in order to form flock and create density gradient between liquid and suspended solid phase (to reduce zeta potential of suspended colloidal particles).

Chloride value of the raw effluent was3500 mg/lit. It was decreases to 2821 mg/lit, 2735 mg/lit, 2613 mg/lit., 2521 mg/lit, and 2405 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, and 50 mg/lit. of nano adsorbent of $FeSO_4.7H_2O$ respectively Table. 7. The reduction in the chloride value might be due to the replacement of chloride by perchlorate ions in plain sedimentation.

Sulphate value of the raw effluent was 1900 mg/lit. It was decreases to 1725 mg/lit, 1707 mg/lit,1696 mg/lit,1670 mg/lit and 1649 mg/lit. with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit,50 mg/lit of nano adsorbent of $FeSO_4.7H_2O$ respectively Table. 7. The reduction in the sulphate value might be due to the oxidation of sulphate form into elementary sulphur, which formed flocculation and undergo plain sedimentation.

The BOD of the raw effluent was 600 mg/lit and decreases to 492 mg/lit, 450 mg/lit , 430 mg/lit, 417 mg/lit, and 402 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit,50 mg/lit of nano adsorbent of $FeSO_4.7H_2O$ respectively Table.

7. The decrease in BOD might be due to coagulating effect of the complex with bio organic compounds. It is evident that heavy metals are toxic to aquatic microorganisms beyond certain concentration.

The COD value of the raw effluent was 3400 mg/lit and decrease to 2688 mg/lit, 2640 mg/lit, 2616 mg/lit, 2593 mg/lit, and 2574 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit,50 mg/lit. of complexes respectively Table. 7. This reduction in COD might be due to nitrogenous increment in waste water by addition of dosed nano adsorbent of $FeSO_4.7H_2O$.

Alkalinity of the raw effluent was 7000 mg/lit and decrease to 6132 mg/lit, 6109 mg/lit, 6094 mg/lit, 6079 mg/lit, and 6050 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit,50 mg/lit of nano adsorbent of $FeSO_4.7H_2O$ respectively Table. 7.

The total hardness of the raw effluent was 4500 mg/lit and decrease to 3725 mg/lit, 3520 mg/lit, 3415 mg/lit, 3211 mg/lit, and 3113 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of nano adsorbent of $FeSO_4.7H_2O$ respectively Table. 7.

Calcium value of the raw effluent was 3000 mg/lit and decrease to 2310 mg/lit, 2262 mg/lit, 2174 mg/lit, 2033 mg/lit, and 1983 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of nano adsorbent of $FeSO_4.7H_2O$ respectively Table. 7.

Magnesium value of the raw effluent was 900 mg/lit and decrease to 834 mg/lit, 815 mg/lit, 793 mg/lit, 784 mg/lit, and 762 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of nano adsorbent of $FeSO_4.7H_2O$ respectively Table. 7.

Sulphide value of the raw effluent was 27 mg/lit and decrease to 19 mg/lit, 15 mg/lit, 13 mg/lit, 10 mg/lit, and 9 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of nano adsorbent of $FeSO_4.7H_2O$ respectively Table. 7.

Phosphate value of the raw effluent was 1.59 mg/lit and decrease to 1.03 mg/lit, 0.95 mg/lit, 0.81 mg/lit, 0.62 mg/lit, and 0.53 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of nano adsorbent of $FeSO_4.7H_2O$ respectively Table. 7.

Sodium value of the raw effluent was 800 mg/lit and decrease to 713 mg/lit, 685 mg/lit, 661 mg/lit, 632 mg/lit, and 614 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of nano adsorbent of $FeSO_4.7H_2O$ respectively Table. 7.

Table.6: Characterization of Dye effluent with $CuSO_4.5H_2O$ nano particles

S.NO	Parameters	Unit	Raw Sample	10 mg/L	20mg/L	30mg/L	40 mg/L	50 mg/L
1.	pH at 25°C	Number	8.5	8.5	8.8	9.0	9.2	9.8
2.	Total Dissolved solids at 180°C	Mg/L	15,216	12,300	12,000	11,700	11,100	10,400
3.	Chlorides as Cl	Mg/L	3500	2400	2325	2240	2180	2100
4.	Sulphide as SO_4	Mg/L	1900	4239	4180	3972	3680	3379
5.	BOD (at 27°C for 3 days)	Mg/L	600	430	425	415	405	400
6.	COD	Mg/L	3400	3200	3120	3040	2970	2880
7.	Alkalinity	Mg/L	7000	6200	6175	6150	6120	6100
8.	Total hardness	Mg/L	4500	6500	6460	6400	6340	6300
9.	Calcium	Mg/L	3000	1400	1384	1372	1367	1362
10.	Magnesium	Mg/L	900	729	717	702	693	680
11.	Sulphide	Mg/L	27	12	11	10	9	8
12.	Phosphate	Mg/L	1.59	0.62	0.58	0.47	0.35	0.33
13.	Sodium	Mg/L	800	900	885	872	861	840
14.	Potassium	Mg/L	30	25	17	14	13	11
15.	Nitrate	Mg/L	5.10	2.37	2.12	1.82	1.74	1.60

Table. 7: Characterization of Dye effluent with $FeSO_4.7H_2O$ nano particles

S.NO	Parameters	Unit	Raw Sample	10 Mg/l	20 Mg/l	30 Mg/l	40 Mg/l	50 Mg/l
1.	pH at 25 °C	Number	8.5	8.8	9.0	9.1	9.1	9.4
2.	Total Dissolved solids at 180 °C	Mg/L	15,216	13,172	13,041	12,840	12,520	12,163
3.	Chlorides as Cl	Mg/L	3500	2821	2735	2613	2521	2405
4.	Sulphide as SO_4	Mg/L	1900	1725	1707	1696	1670	1649
5.	BOD (at 27 °C for 3 days)	Mg/L	600	492	450	43017	402	
6.	COD	Mg/L	3400	2688	2640	2616	2593	2574
7.	Alkalinity	Mg/L	7000	6132	6109	6094	6079	6050
8.	Total hardness	Mg/L	4500	3725	3520	3415	3211	3113
9.	Calcium	Mg/L	3000	2310	2262	2174	2033	1983
10.	Magnesium	Mg/L	900	834	815	793	784	762
11.	Sulphide	Mg/L	27	19	15	13	10	9
12.	Phosphate	Mg/L	1.59	1.03	0.95	0.81	0.62	0.614
13.	Sodium	Mg/L	800	713	685	661	632	614
14.	Potassium	Mg/L	30	26	23	17	15	12
15.	Nitrate	Mg/L	5.10	4.13	3.87	3.65	3.41	3.12

Potassium value of the raw effluent was 30 mg/lit and decrease to 26 mg/lit, 23 mg/lit, 17 mg/lit, 15 mg/lit, and 12 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of nano adsorbent of $FeSO_4.7H_2O$ respectively Table. 7.

Nitrate value of the raw effluent was 5.10 mg/lit and decrease to 4.13 mg/lit, 3.87 mg/lit, 3.65 mg/lit, 3.41 mg/lit, and 3.12 mg/lit with the addition of 10 mg/lit., 20 mg/lit., 30 mg/lit., 40 mg/lit, 50 mg/lit of nano adsorbent of $FeSO_4.7H_2O$ respectively Table. 7.

CONCLUSION

From this study, we concluded that the retardation of chemicals from coloured effluents of dye industry and tanneries adsorption on metal nano particles useful for controlling water pollution. It was confirmed that higher removal of physico chemical pollutants from dye effluents adsorbent dose of more than 50mg/L was favorable. Even though the removal efficiency of these three metal nano particles ($MgSO_4,$ $CuSO_4.5H_2O$ and $FeSO_4.7H_2O$) are not much higher than other adsorbents, but in this method easy synthesis process of nano particles as well as chemicals used for this method easily available and very cheap. An attempt made to surroundings pleasant adsorbent big chemical pollutants elimination may be executed. So it may be substituting different pricey adsorbents. With the experimental data acquired in this study, it's far viable to design and optimize an economical treatment manner for the undesirable chemical compounds elimination from commercial effluents.

REFERENCES

1. Neamtu. M., Siminiceanu I., Yediler A. and Kettrup A., *Dyes Pigments*, **2002.,** *53,* 93.
2. Jumaasiam. A., Chuab T.G., Gimbon J., Choong T.S. and Azmi I., *Desalination*, **2005.,** *186,* 57.
3. Setamanit S., Fongasatitul P. and Sivadechathep J., *ASEAN Acheivement and Future Directions in Pollution Control, Ministry of Science Tech. and Environ., Thailand*, **2002,** *27,* 33.
4. Janas P., Buchtora H. and Ruzmarava M., *Water Res.,* **2003,** *37*, 4938.
5. Mall I.D. and Upadhyay S.N., *Indian J. Environ. Hlth.,* **1998,** *40* **,** 177.
6. Chen C.C., LiaU H. J., Cheng C.Y., Yen C.Y. and Chung Y.C., *Biotechnol. Lett.,* **2007,** *29* **,** 391
7. Saha P., Chowdhury S., Gupta S., Kumar I. and Kumar R., *Clean : Soil Air, Water.,* **2010,** *38*(56) 437 .
8. Rochat J., Demenge P. and Rerat J.C., *Toxicol. Eur. Res.,* **1978** ., *1* **.,**23.
9. Adamson A.W.,"*Physical chemistry of surfaces,"Inter Science publ.Inc., New york*, **1960**
10. Mckay G. , Oterburn M.S. and Sweeney A.G., *Water Res.,* **1980,** *14*, 15.
11. Ho, Y.S., Porter, J.F., McKay, G.,. *Water Air Soil Pollution*, **2002,** *141*, 1–33.