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Removal of Lignin from aqueous solution using Fe_3O_4 Nanoparticles as an effective adsorbent

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ABSTRACT:
The study was carried out to find out the adsorption efficiency of lignin from paper mill waste water by using Fe_3O_4 magnetic nanoparticles. The physico-chemical analysis of paper mill effluent results high B.O.D value. Separations of lignin from black liquor were done by acid precipitation method and removal of lignin was done with nanoparticles. Synthesis of nanoparticles was done by co-precipitation method by mixing and stirring of $FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ solution at 2:1 molar ratio. The nanoparticles were characterized by using U.V-Vis spectrophotometer and X-Ray Diffraction. U.V-Vis spectra show absorbance spectra at around 585 nm while XRD revealed around 10 nm sizes of Fe_3O_4 MNPs. The removal efficiency of lignin by Fe_3O_4 MNPs was investigated at different pH and contact time. Maximum adsorption of lignin onto the surface of Fe_3O_4 MNPs took place at pH 2.5 and 10 mins of contact time. Desorption of lignin by nanoparticles was studies by using different organic solvents.
Key words: Adsorption, Desorption, Lignin, Nanoparticles, U.V-Vis spectrophotometer and X-Ray Diffraction and.

I. INTRODUCTION:

Huge amount of wastewater effluent generated from paper mill industry is discharged into running water or on agricultural land. 75-95 % of the waste water discharge by paper industries contains organic and inorganic pollutants which causes negative impact on environment [1]. Exposure of industrial effluent can delay, retard and decline in germination and seedling growth [2]. Another study found that paper mill effluent affected germination of rice, black gram and tomato seeds but enhance the growth when exposed to diluted form of effluent [3]. Diluted effluents showed negligible effect on the overall growth of pigeon pea seedling when exposed to paper mill effluent [4]. Physiotoxicity of the paper mill effluents was also observed in *Elusine coracana* and *Oryza sativa* crops [5, 6 and 7]

Huge quantity of lignin is produced in Kraft pulping industries but more than 99 % is burned and cannot be recovered for industrial uses [8]. It has been reported that 50-106 tons of lignin that are produced as a by-products from pulp and paper industry are burned; only small amounts of it is used as additives in industries. The lignin can be a substitute to expensive petrochemicals which is used in the production of engineering plastics [9, 10 and 11]

Magnetic nanoparticles synthesis has become an important area of research due to its application in advance magnetic materials, high density magnetic recording media, catalyst and medical diagnostics [12, 13 and 14]. Magnetic nanoparticles have vast environmental application particularly in cleaning up contaminated soil and ground water. It is due to its small size which is much more effective than the conventional iron powders [15]. Iron oxide nanoparticles have scientific and technological interest due its ability to undergo dispersion in different media. Magnetite (Fe_3O_4), maghemite (γ - Fe_2O_3) and hematite (α-Fe_2O_3) are the different iron oxide forms in nature. Magnetite (Fe_3O_4) is considered as ideal candidate for biological application like tag for sensing and imaging and activity agent for antitumor therapy [16, 17 and 18]

II. MATERIALS AND METHOD:

2.1 Study area:

The study area falls under Morigaon district of Assam. The samples, i.e., the paper mill effluents were collected from one of the two drains carrying Paper Mill Effluent (PME) to *Elenga beel* which after flowing a distance of 25 Km downstream meet River Kalong. The sample was collected 0.5 Km towards North-west from the released site (Fig 1) to study the physico-chemical properties. The study was carried out during April 2014 to March 2015.

2.2 Sampling:

The wastewater effluents were collected in plastic container which was previously cleaned with non ionic detergent and then rinsed with tap water. It was later soaked in 10% HNO_3 and then rinsed with distilled water. The effluent samples were subject to physico-chemical analysis by using standard methods.

2.3 Synthesis of Magnetic nanoparticles:
All chemicals used in this study were of analytical grade. Ferric chloride hexahydrated ($FeCl_3.6H_2O$) and Ferrous chloride tetrahydrated ($FeCl_2.4H_2O$) and Ammonium hydroxide were purchased from Aldrich chemicals. Fe_3O_4 nanoparticles were prepared by co-precipitation method with slight modification [19]. The Fe_3O_4 magnetic nanoparticles were further characterized by using U.V-Vis spectrophotometer and X-Ray Diffraction.

2.4 Removal of lignin from black liquor:
Lignin samples were separated from black liquor by acid precipitation method with dilute sulphuric acid solution [20]. After completion of precipitation, the sample were filtered with filter paper and finally dried in hot air oven at 100ºC. A standard stock solution of lignin (1000 mg/L concentration) was prepared in double distilled water. Separation of lignin from aqueous solutions was done by diluting lignin solution with distilled water and adding Fe_3O_4 Magnetic Nanoparticles under optimized conditions [21].
2.5 Lignin adsorption using MNPs:
Stability of lignin solution (100 mg L^{-1}) was studied at various pHs and contact time. The adsorption spectrum of lignin was studied at 280 nm. All optimization studies were carried out according to the procedure given by Mostashari *et al.,* 2012. The removal efficiency of lignin by Fe_3O_4 Magnetic Nanoparticles was calculated according to the following equation:

$$\text{Lignin removal efficency } (\%) = \frac{\text{Co} - \text{Cr}}{\text{Co}} \text{x } 100$$

where C_0 and Cr are the initial and residual concentrations of lignin in the solution (mg L^{-1}), respectively.
2.6 Desorption study:
Desorption of lignin from Fe_3O_4 MNPs was studied at different pH (2.0-3.0) and contact time (1-30 min) by using distilled water, acetonitrile, ethanol and methanol. The study was carried out according to the procedure given by Mostashari *et al.,* 2012.

III. RESULT AND DISCUSSION:

3.1 Physico-chemical analysis:
The waste water effluents discharge from the paper mill easily penetrate to the nearby cultivate land. A few physico-chemical parameters were selected for the assessment of waste water was given in Table 1. Colour is usually the first contaminant to be recognized in wastewaters which affects the transparency and gas solubility [22]. The colour of the effluent from paper industry was dark brown having unpleasant smell. The collected samples recorded the pH value of 8.71 ± 0.3 which is slightly alkaline in nature. WHO guidelines suggest the tolerance pH limit of paper mill wastewater as 6-9 [23]. It was probably due to the presence of lignin and their derivatives in water bodies. Temperature is also one of the important factors that affect the properties of waste water. The average temperature of paper mill effluent was found to be 30 ± 5°C. The Electrical Conductivity value of effluent sample was found to be 2.5 ± 0.11 dSm^{-1}. The higher value of pH and Electrical conductivity were due to impact of industrial effluents from paper mill to the water bodies [24].
The B.O.D and C.O.D value of the effluent sample was found to be 403 ± 30.2 mg/L and 556 ± 25.7 mg/L respectively. As per WHO guideline the permissible limit of BOD and COD value of industrial effluent are 50 mg/L and 1000 mg/L respectively [23]. The higher BOD value indicates high pollution level of the waste water effluents. However, the COD value of paper mill effluent is below WHO recommended level. Presence of both biodegradable and non-biodegradable pollutants in waste water increases the B.O.D and C.O.D value. Continuous disposal of waste water over the year from paper industry to water bodies increases the pH and alkalinity of water. Water discharge (nearly 75-90%) from paper mill industries contains organic, inorganic pollutants and colouring materials. As a result it directly affects soil and which alters plant growth and development [1 and 25]. The Total Dissolved Solid and Total Solid Suspended value of the samples were found to be 1353 ± 32.0 mg/L and 3.94 ± 0.08 mg/L respectively.

3.2 Characterization of Nanoparticles
Fe_3O_4 MNPs were synthesized by co-precipitation method. The reaction parameters were systematically balanced so as to produce designed nanoparticles. $FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ solution were prepared in 50 ml beaker at 2:1 molar ratio. It was heated at 70°C for 10 min. After heating it was precipitated with Ammonia solution (Fig 2). The Black precipitate was separated with strong magnet and it was dried in hot air oven at 100° C for overnight. The characterization of synthesized nanoparticles was done by U.V-Vis spectrophotometer and X-Ray Diffraction. The optical absorption spectra of iron nanoparticles were recorded by using Hitachi, Model no.3210. U.V-Vis spectra showed absorbance spectra at around 585 nm (Fig 3). The spectra were found quite sensitive to form nanoparticles because it exhibited an absorption peak due to the surface Plasmon. Similar peak was also observed during synthesis of iron nanoparticles by slow chemical reduction method [26].
The XRD pattern of iron nanoparticles samples were recorded at X-Ray Diffractometer (Model-XPERT PRO). Figure 4 shows the XRD pattern of samples with 2Ɵ ranging from 30º to 40º resulting in

formations of iron nanoparticles. Same result was also obtained by Saha and Bhunia, 2013 when they synthesized nanoparticles with chemical reduction methods. X-ray Diffraction technique was used to identify the desired nanoparticles prepared by co-precipitation method with ferric and ferrous salts, with 2Θ ranging from 30º to 80º. The nanoparticles sizes were determined by Scherer's formula:

$$D = \frac{K\lambda}{b}\cos\theta$$

The diffraction peaks corresponding to (311), (511) and (440) are identical to characteristics peak of the Fe_3O_4 MNPs. The characteristic peak of Fe_3O_4 MNPs shows cubical spinal structure. Same identical peak was found when Fe_3O_4 MNPs were synthesized with co-precipitation method [19]. The application of Scherer's formula to the (311) reflection peak showed around 10 nm sizes of Fe_3O_4 MNPs which is similar to the result obtained by Kulkarni et al., 2012.

3.3 Separation of lignin from Black liquor

Separations of lignin from black liquor were done from standard stock solutions by acid precipitation method. Lignin attained negative charge due to disassociation of phenolic and carboxyl groups on alkaline environment during acid precipitations. Lignin molecules attain stability after they repel each other by electrostatic force of attractions. The hydrogen ions interact with negatively charge lignin at low pH and finally neutralize the charge. Finally the repulsive force reduced and results in precipitation of lignin [27]. However, in the present study, small amount of lignin was detected in wastewater effluents.

3.4 Effect of pH and contact time on the adsorption efficiency

A series of adsorptions experiment were conducted by mixing lignin solution with Fe_3O_4 MNPs for optimizing the condition such as pH and contact time. The effect of pH in the range of 2-7 is shown in Fig 5, indicating that the adsorption decrease with increase in pH. At acidic pH, the Fe_3O_4 MNPs has a positive charge on its surface which favors the adsorption process. Positive charge density of Fe_3O_4 MNPs decreases with increase in pH [28 and 29]. Electrostatic attraction between positive charge Fe_3O_4 MNPs and negative charge lignin decreased with increase in pH value. It was observed that after pH 3.0, the charge density on the surface of adsorbent decreased. pH 2.5 was selected for adsorption experiment due to maximum adsorption of lignin onto the surface of Fe_3O_4 MNPs.

In order to determine the effect of contact time on lignin removal by using Fe_3O_4 MNPs further experiments were carried out at room temperature and pH 2.5 with the contact time varying in the range of 1-120 min. Fig 6 shows the effect of contact time on the adsorption percentage of lignin. It is clear that the adsorption rate of lignin were time dependent. The results showed that adsorption of lignin increased with contact time up to 5 min. The optimum contact time where maximum removal of lignin by nanoparticles took place at 10 min. Similar result was also obtained when lignin was absorbed by magnetic nanoparticles [21]. For instance the adsorption efficiency of lignin was 65% at contact time of 5 min, but it increased to 80% at 10 min. It is very interesting to observe that the adsorption rate of lignin was high and remained nearly constant at the range of 10-120 min of investigation.

3.5 Desorption of Lignin

It is possible to regenerate or reuse Fe_3O_4 MNPs because lignin adsorption onto Fe_3O_4 MNPs is a reversible process. The result (Fig. 7) showed that desorption efficiency of Acetonitrile above 80 % could be achieved at pH 2.5 within 10 min contact time. At pH 2.0, desorption efficiency of Acetonitrile was below 80 %. However at pH 3.0, the desorption efficiency of distilled water, ethanol and methanol were lowered than 50 % compared to Acetonitrile at different contact time (0-30 min). Desorption of lignin using different organic solvents was found to be high at pH 2.5 with 10 min of contact time. Among solvents the acetonitrile showed the highest desorption efficiency. Same results were also obtained by Mostashari *et al.*, 2012, when desorption of lignin took place with Fe_3O_4 MNPs.

IV. Figures and Tables:

Fig 1: Sample collections site near paper mill, Morigaon, Assam.

Fig 2: Synthesis of Fe_3O_4 Magnetic nanoparticles by Co-precipitation method

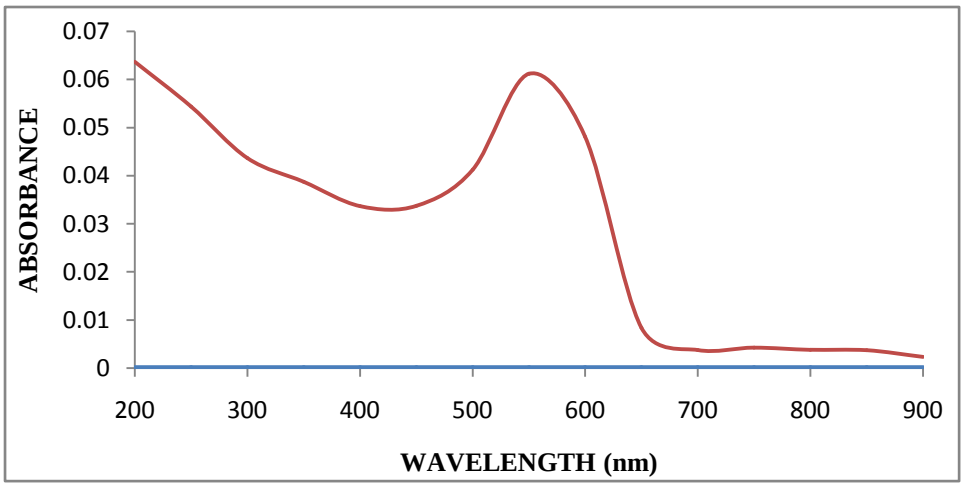

Fig 3: Absorption spectra of Iron nanoparticles

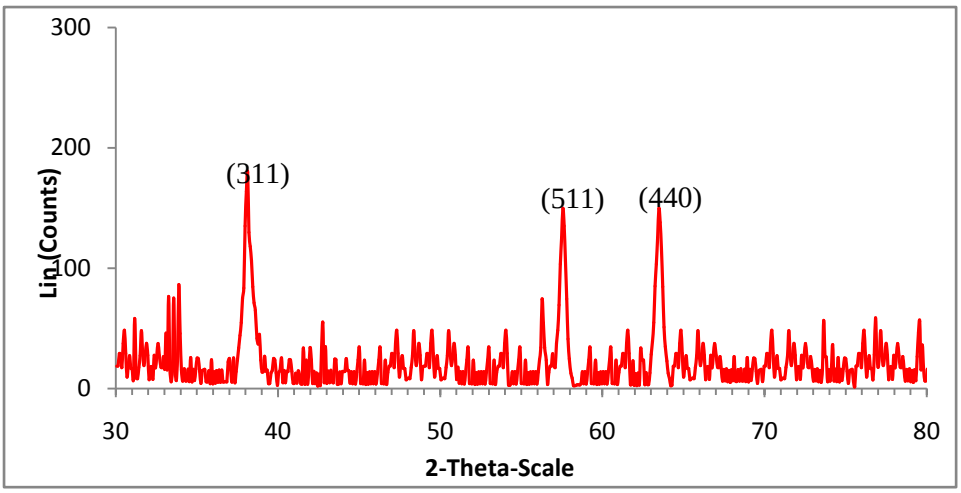

Fig 4: XRD pattern of Fe_3O_4 MNPs

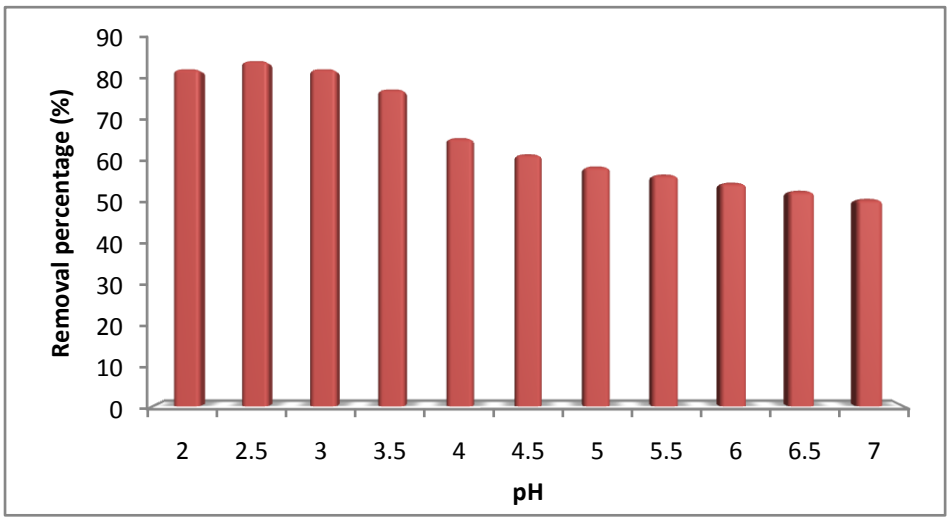

Fig 5: The effect of different pH on the adsorption of lignin using Fe_3O_4 MNPs

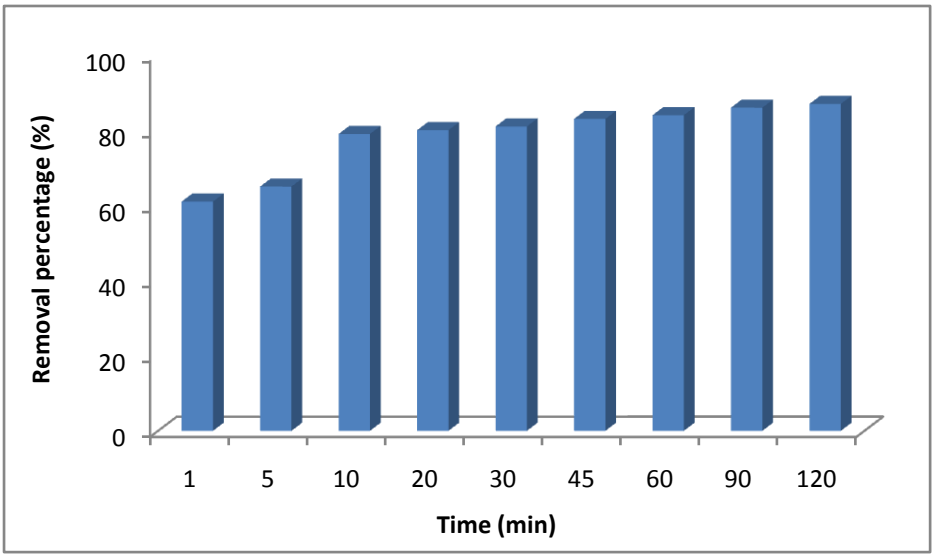

Fig 6: The effect of different contact time on the adsorption of lignin using Fe_3O_4 MNPs

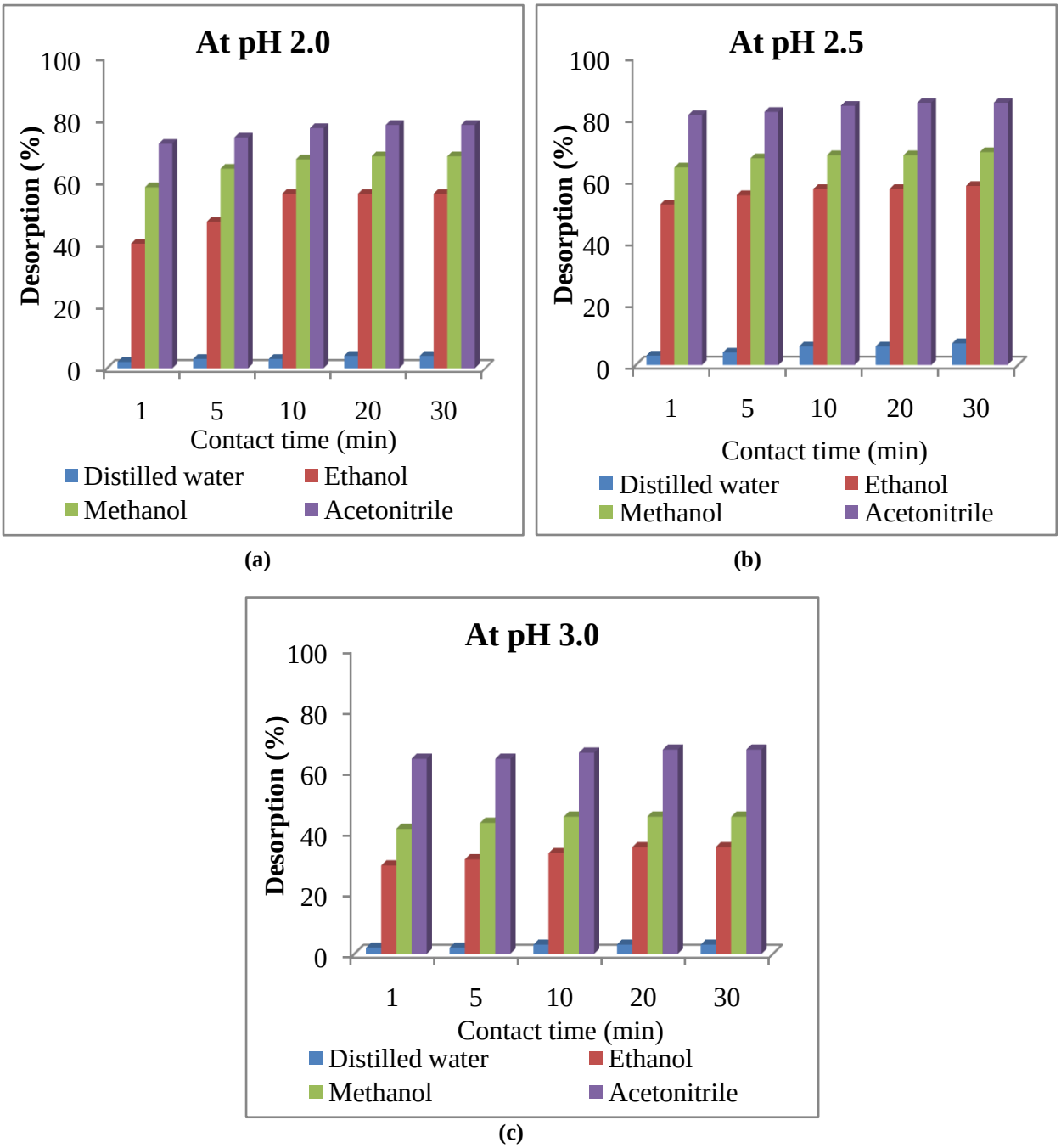

Fig 7: Desorption of lignin from Fe_3O_4 MNPs at (a) pH 2.0, (b) pH 2.5 and (c) pH 3.0

Table 1: Physico-chemical studies industrial effluents (Mean value ± SD):

Character	**Particulars**
pH	8.71 ± 0.3
Colour	Dark brown
Odour	Unpleasant
Temp (°C)	28 ±3
Electrical conductivity (dS m^{-1})	2.5±0.11
B.O.D (mg/mL)	403±30.2
C.O.D (mg/mL)	556±25.7
TDS (mg/mL)	1353±32.0
TSS (mg/mL)	3.94±0.08

V. Conclusion:

From the study it may be concluded that the paper mill effluent not only impact the water quality but also directly destabilize the ecosystems. In this study, we reported chemical co-precipitation approach for synthesizing Fe_3O_4 MNPs which is simple and effective technique. U.V-Vis absorbance and XRD results showed formation of nanoparticles with approximately 10 nm size. Fe_3O_4 MNPs can be used as an efficient sorbent for removal of lignin from aqueous solution. Interestingly, Fe_3O_4 MNPs can also be recoverable by using organic solvent such as acetonitrile. Fe_3O_4 MNPs can be easily synthesized and can be regenerated in short times.

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References:

[1] B.K. Baruah, D.Baruah and M. Das, Sources and characteristics of paper mill effluent. *Env. Eco.*, ***14,*** 1996. 686 - 689.

[2] B.K. Baruah and M. Das, Effect of paper mill effluent on seed germination of crop plant Oryza sativa L. *Environ. Ecol*., ***15,*** 1997, 904-906.

[3] G. Rajannan and G. Oblisami, Effect of paper factory effluent on soil and crop plant. *Ind. J. Environ. Health*. ***21,*** 1979, 120-130.

[4] S.M. Karande and N.A. Ghanvat, Effect of untreated effluents of Provara pulp and paper and distillery on seed germination and early seedling growth in Pigeon pea. *Proc. Acad. Environ. Biol.*, ***3***, 1994, 165-169.

[5] R.N. Mishra, G.N. Panigrahy and K.S. Patra, Studies on physiotoxicity of paper mill effluent on *Elusine coracana* Var. AK p-2. Bull. *Pure and Appl. Sci.*, ***8B,*** 1989, 6-10.

[6] R.N. Mishra, G.N. Panigrahy and K.S. Patra, Studies on physiotoxicity of paper mill effluent on Oryza sativa L. var IR 36. *Bionature*, ***11,*** 1991, 99-101.

[7] R.N. Mishra and P.K. Behera, The effect of paper industry effluent on growth, pigment, carbohydrate and protein of rice seedlings. *Environ. Pollut.*, ***72,*** 1991, 159-168.

[8] E. K. Pye, 2008. Industrial Lignin Production and Applications, *Biorefineries-Industrial Processes and Products*, Wiley-VCH Verlag GmbH.

[9] S. S. Kelley, W. G. Glasser and T. C. Ward, "Lignin: Properties and Materials", *ACS*, ***397***, 1989, 402-413.

[10] O. Milstein, R. Gersonde, A. Huttermann, M. J. Chen and J. J. Meister, Fungal biodegradation of lignopolystyrene graft copolymers. *Appl. Environ. Microbiol*., ***58 (10),*** 1992, 3225-3232.

[11] M. J. Chen, D. W. Gunnells, D. J. Gardner, O. Milstein, R. Gersonde , H.J. Feine, A. Huttermann, R. Frund, H.D. Ludemann and J. J. Meister, Graft Copolymers of Lignin with 1-Ethenylbenzene. 2. Properties, *Macromolecules*, ***29 (5)***, 1996, 1389-1398.

[12] F. Caruso, M. Spasova, A. Susha, M. Giersig and R. A. Caruso, Magnetic nanocomposite particles and hollow spheres constructed by a sequential layering approach, *Chem. Mater.*, ***13,*** 2001, 109-116.

[13] K. Woo, H. J. Lee, J. P. Ahn and Y. S. Park, Sol–gel mediated synthesis of Fe_2O_3 nanorods, *Adv. Mater,*. ***15,*** 2003, 1761-1764.
[14] R. Das and S. Saha, Electrical and chemical characteristics of Ta_2O_5 gate dielectrics on ge-rich SiGe hetarolayers, *Journal of Physical Sciences*, ***16,*** 2012, 177-184.
[15] M.A Abdalla, M.H Jaafar, Z.A. Al-Othman, S.M. Alfadul and M.A. Khan., New route for preparation and characterization of magnetite nanoparticles, *Arabian Journal of Chemistry*, ***4***, 2011, 235–237.
[16] U. Hafeli, W. Schutt, J. Teller and M. Zborowski, *Scientific and clinical application of magnetic carriers, 1st edn, New York, Plenum*, 1997.
[17] J. M. Perez, F. J. Simeone, A. Tsourkas, L. Josephson and R. Weissleder, Peroxidase substrate nanosensors for MR imaging, *Nano Letters*, ***4***, 2004, 119-122.
[18] S. Saha, Growth of PbS Nano Particle and its effect on protein, *Journal of Physical Sciences*, ***16,*** 2012, 217-219.
[19] S.A Kulkarni, P.S. Sawadh and K.K. Kokate, Synthesis and characterization of Fe_3O_4 Nanoparticles for Engineering Applications, *International Conference on Benchmarks in Engineering Science and Technology ICBEST 2012, Proceedings published by International Journal of Computer Applications*, 2012, 17-18.
[20] H. Theliander, The Ligno Boost process: Solubility of lignin. *International Chemical Recovery Conference 29th March - 1st April 2010 Williamsburg, VA, USA.* 33-42.
[21] S. M. Mostashari, S. Shariati and M. Manoochehri, Lignin removal from aqueous solutions using Fe_3O_4 magnetic nanoparticles as recoverable adsorbent, *Cellulose Chem. Technol*., ***47 (9-10)***, 2013, 727-734.
[22] W. Yuxing and Y and Jain , Decolourisation of synthetic dyes and waste waters from textile, *Water Research*, ***33 (16),*** 1999, 3512-3520.
[23] J.C. Akhan, Physicochemical determination of pollutant in waste water and vegetable samples along the Jakara wastewater Channelin Kano Metropolis, Kano State, Nigeria, *European Journal of Scientific Research*, ***23,*** 2008, 122-123.
[24] D.K. Deka, Industrial Waste Threaten Environmental Quality of Jiong beel, *Biological Forum – An International Journal*, ***5(1),*** 2013, 109-112.
[25] U.J. Medhi, A.K. Talukdar, S.Deka, Impact of paper mill effluent on growth and development of certain agricultural crops. *J. Environ. Biol.* ***32,*** 2011, 185-188.
[26] S. Saha and A. K. Bhunia, Synthesis of Fe_2O_3 Nanoparticles and Study of its Structural, Optical Properties, *Journal of Physical Sciences, **17**, 2013, 191-195.*
[27] G. Wang and H. Chen, Fractionation of alkali-extracted lignin from steam-exploded stalk by gradient acid precipitation. *Separation and Purification Technology*, ***105,*** 2013, 98-105.
[28] X. Zhao, Y. Shi, T. Wang, Y. Cai and G. Jiang, Preparation of silica-magnetite nanoparticle mixed hemimicelle sorbents for extraction of several typical phenolic compounds from environmental water samples, *Journal of Chromatography .A*, ***1188 (2)***, 2008, 140-147.
[29] K. R. Ramakrishna and T. Viraraghavan, Use of slag for dye removal, *Waste Management.*, ***17(8),*** 1997, 483-488.