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Amputation of noxious organic pollutant from aqueous system using Mn-Zn ferrite nanocomposite

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Abstract
Mn-Zn ferrite bio-nanocomposites was synthesized from Tulsi leaves activated carbon. The Tulsi leaves activated carbon is made by placing the dried leaves by the help of sunlight. After dried we crushed leaves to make it in a powder form. Then leaf powder and place in a muffle finance to make an activated carbon with temperature up to 800 °C for 2 hours in a muffle furnace. After 2 hours an activated carbon is be formed. The solution mixture then refluxes with magnetic stirrer for about 5hrs. Then filter out nanocomposite and dry them. The synthesized bio-nanocomposite, activated carbon and bio material is confirmed by the FTIR spectroscopy. We used methyl orange dye to check the adsorption quality of bio nano composite. We perform four parameters like concentration of dye, concentration of BNC, effect of pH and contact time and confirmed it by the help of UV spectroscopy.

Keywords: Amputation, noxious organic pollutant, aqueous system, Mn-Zn Ferrite, nanocomposite

Introduction
Water pollution caused due to the addition of heavy metals resulting from the industrial activities is increasing tremendously and is a matter of global concern**.** Mining, mineral processing and metallurgical operations are generating effluents containing heavy metals. The heavy metals present in the waste-water are persistent and non-degradable in nature.

Moreover, they are soluble in aquatic environment and thus can be easily absorbed by living cells. Thus, by entering the food chain, they can be bio-accumulated and biomagnified in higher trophic levels also. The conventional methods for heavy metal removal from waste water includes chemical precipitation, chemical oxidation, ion exchange, membrane separation, reverse osmosis, electro dialysis etc [1]. These methods are not very effective, costly and require high energy input.

Adsorption has emerged out to be better alternative treatment method. It is said to be effective and economical because of its relatively low cost. The key benefit of adsorption method for heavy metal removal is less initial as well as operation cost, unproblematic design and less requirement of control systems. Generally, the heavy metals are present in the waste water at low concentrations and adsorption is suitable even when the metal ions are present at concentrations as low as 1mg/l. This makes adsorption an economical and favorable technology for heavy metal removal from wastewater [2].

Biosorption is a property of certain types of inactive, dead microbial biomass to bind and concentrate pollutants from every aqueous solution. Biosorption is defined as the accumulation and concentration of organic and inorganic pollutants including metals, dyes and odor causing substances from aqueous solutions by the use of biological materials.

The main objective is to study the effect of Tulsi (*Ocimum Sanctum*) on removal of heavy metals- mercury and lead [3]. The biocarbon obtained from medicinal plant called *Ocimum* sanctum is considered as a cheap material for the removal of metal ions like lead, cadmium, copper, zinc, nickel etc. from aqueous solution. The activated biocarbon Tulsi was investigated as replacement for the current expensive methods of removing metal ions from aqueous solutions. Tulsi extracts are used in ayurvedic remedies for common colds, headaches, stomach disorders, inflammation, heart disease, various forms of poisoning and malaria. Traditionally, Tulsi is taken in many forms, as herbal tea, dried powder or fresh leaf. Several recent investigations using these extracts indicate anti-inflammatory, antioxidant and immune modulatory and antistress properties [4]. In addition, it has been reported to have radio protective and anti-carcinogenic property. Several medicinal properties have been attributed to Tulsi. Tulsi is known as a general vitalizer and increases physical endurance.

Activated carbons are extremely versatile adsorbents and have major industrial significances. They have high specific porosity and hence enhanced surface area. Thus, they are used in wide range of applications concerned particularly with the removal of species by adsorption from the liquid or gas phase. Activated carbons can be considered to be composed of non-graphitic, non-graphitize able carbons with a highly ordered microstructure.

Bio-nanocomposites may be considered as a variety of nanocomposites. It accounts for the presence of dispersed particles of which at least one dimension is in the nanometer range. None the less, the profound distinctions of biopolymers from synthetic, petroleum-based polymers do not allow identifying bio-nanocomposites with the nanocomposites. They differ in the solubility in water, thermal stability, and biocompatibility, and biodegradability, which determine the methods of preparation, functionalities, and areas of applications of materials. The bio-nanocomposites are composite materials that contain constituent(s) of the biological origin and particles with at least one dimension in the range of 1–100 nm.

Adsorption, capability of all solid substances to attract to their surfaces molecules of gases or solutions with which they are in contact. Solids that are used to adsorb gases or dissolved substances are called adsorbents; the adsorbed molecules are usually referred to collectively as the adsorbate. An example of an excellent adsorbent is the charcoal used in gas masks to remove poisons or impurities from a stream of air. Adsorption refers to the collecting of molecules by the external surface or internal surface (walls of capillaries or crevices) of solids or by the surface of liquids. Absorption, with which it is often confused, refers to processes in which a substance penetrates into the actual interior of crystals, of blocks of amorphous solids, or of liquids. Sometimes the word sorption is used to indicate the process of the taking up of a gas or liquid by a solid without specifying whether the process is adsorption or absorption [5].

Biosorption has been defined as a passive physical-chemical process that biomolecules of non-living biological material, refer as biosorbent, bind with heavy metal ions from aqueous solutions. It is classified as an alternative sustainable remediation technology in terms of resource and environmental impacts where the biosorbent is biodegradable based material and the heavy metal in dilute acid could be extracted via electrolysis [6-7]. Biosorption offers the advantages of low cost, effectiveness for dilute effluents, minimum chemicals usage and reduced toxic sludge generation.

Nano technology refers to the branch of science and engineering devoted to designing, producing, structures and using, devices, and systems by manipulating atoms and molecules at nanoscale, i.e. having one or more dimensions of the order of 100 nanometres (100 millionth of a millimetre) or less. Many of the applications of nanotechnology involve new materials that have very different properties and new effects compared to the same materials made at larger sizes. This is due to the very high surface to volume ratio of nanoparticles compared to larger particles, and to effects that appear at that small scale but are not observed at larger scales [8-9].

Depending on the source of emission, highly problematic waste materials produced in massive amounts can be classified into wastes generated by industries, and wastes generated by consumers. From the industrial sector, large batteries, rubber tires, wastewater, and bio solids are prominent sources of carbon, lead, zinc, copper, and palladium.

Synthesis and Methodology

Materials Required: All reagents such as manganese chloride, zinc chloride, iron chloride and distilled water which were used throughout the research work. Equipment is analytical balance, magnetic stirrer, muffle furnace, hot air oven, hot plate, UV spectrophotometer, IR apparatus etc.

Collection of biomaterial: The leaves of Tulsi plant was collect and then wash with distilled water to remove impurities. Then, it was dried for several days in a shaded atmosphere. After that we crush the dry leaves of the Tulsi into the powder form. Now this powder of Tulsi leaves is heated in the muffle furnace at about 800–900 °C temperature for 40-45 minutes in a crucible to make it activated carbon. Hence the activated carbon is prepared.

Chemically modified activated charcoal (CAC): Take 2gm of activated charcoal and add 0.3M PCl_5 solution in 25 ml volume. Put it onto the hot plate for 30 minutes at 60–70 °C. After that cool down the solution and filter out the precipitate which act as chemically modified activated carbon. It helps in opening the pores of activated charcoal (CAC).

Synthesis of manganese zinc ferrite ($ZnFe_2O_4$) nanoparticles: A 0.1 M solution of manganese zinc ferrite nanoparticles was prepared by dissolving manganese chloride, zinc chloride and iron chloride in 30 ml of water. Now add 3M sodium hydroxide (NaOH) solution of 10 ml and stirred for hour with the help of magnetic stirrer along with refluxing at 60-70 °C temperature. Now the mixture containing manganese, zinc and ferric ions were put into the 2M NaOH solution of 10 ml with constant stirring for 3 hours at 60-70 °Cwith refluxing. Now add some more NaOH, the heating process transformed the precipitate precursors into the manganese zinc ferrite nanoparticle. Now dry the precipitate in oven at 70 °C temperature overnight.

Activated charcoal and manganese zinc ferrite ($Mn_{0.4}Zn_{0.6}Fe_2O_4$) nanocomposite (BNC)-Initially chemically activated carbon (2 gm) was dissolved in 30 ml of water on heating, after complete dissolution, 3gm of manganese zinc ferrite nano particle was added to it. Then it was dispersed using magnetic stirrer for 4 hours at 50 °C. The solution was poured into petri dish and the solvent was evaporated at 50 °C overnight, to cast into film. The obtained film was stored in the desiccators to keep out from moisture. The figure (1) represents bionanocomposite.

Fig 1: Bio nanocomposite

Results and Discussions

Fourier transform infrared (FTIR) spectroscopy is a significant analytical method which offers appropriate information on the functional groups and structure of a compound. Since FTIR determines the stretching vibrations of molecules, it can be utilised in the identification of functional groups present in an unknown inorganic and organic compounds.

Ultraviolet (UV) visible spectroscopy is a spectrophotometric technique, which comprises of the measurement of light photons in the UV visible region. UV visible spectroscopy measures the intensity of light before and after it has been passed through the material. So, in this study we use both these techniques for the characterization of the synthesized nanoparticles and nanocomposites. We also synthesize CAC and also characterized it with the help of FTIR. In order to check the properties of BNC synthesized we performed an adsorption experiment from which we observe the absorbance values of BNC synthesized by the help of UV- spectroscopy.

A vibrating-sample magnetometer (VSM) (also referred to as a Foner magnetometer) is a scientific instrument that measures magnetic properties based on Faraday's Law of Induction. Simon Foner at MIT Lincoln Laboratory invented VSM in 1955 and reported it in 1959.

Transmission electron microscopes (TEM) are microscopes that use a particle beam of electrons to visualize specimens and generate a highly-magnified image. TEMs can magnify objects up to 2 million times. In order to get a better idea of just how small that is, think of how small a cell is.

Brunauer-Emmett-Teller (BET) theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of materials. Brunauer–Emmett–Teller (BET) theory is used to measure the surface area of solid or porous materials. It gives important information on their physical structure as the area of a material's surface affects how that solid will interact with its environment.

So, all these techniques are very much useful for characterizing the sample, adsorption capacity, surface area, magnetism, magnified images etc. All these physical properties are very much useful for analysing our synthesized bio-nanocomposite and to check its properties that whether it gives us desired results or not. So, let us discuss each of the technique one by one as follows:

FTIR Analysis

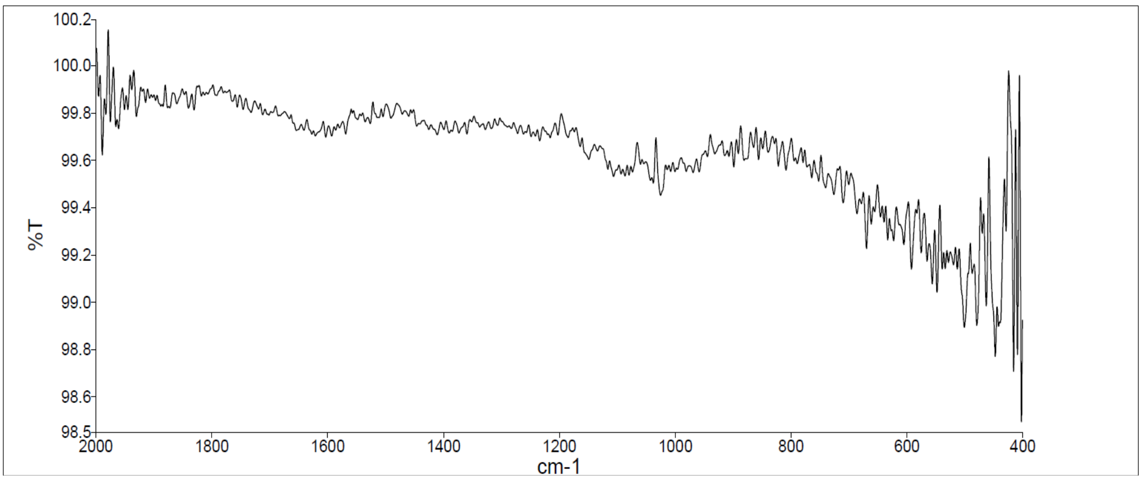

Fig 2: Raw material

FTIR provide the useful information about the structure and bonding present in the synthesized nanocomposites. FTIR spectrum of biomaterial was obtained using a spectrophotometer (PerkinElmer Spectrum). Here in figure (2) as for the case of raw material IR ranges from 2000-400 cm^{-1}. The OH stretching vibration shows a peak at 1990-1950 cm^{-1} range of the spectra. Then carbon double bonded carbon (C=C) shows a peak at 1630-1580 cm^{-1}. Also, C-H wagging peaks comes at 1000-600 cm^{-1} range of the spectra and also C-H bending at 900-700 cm^{-1}.

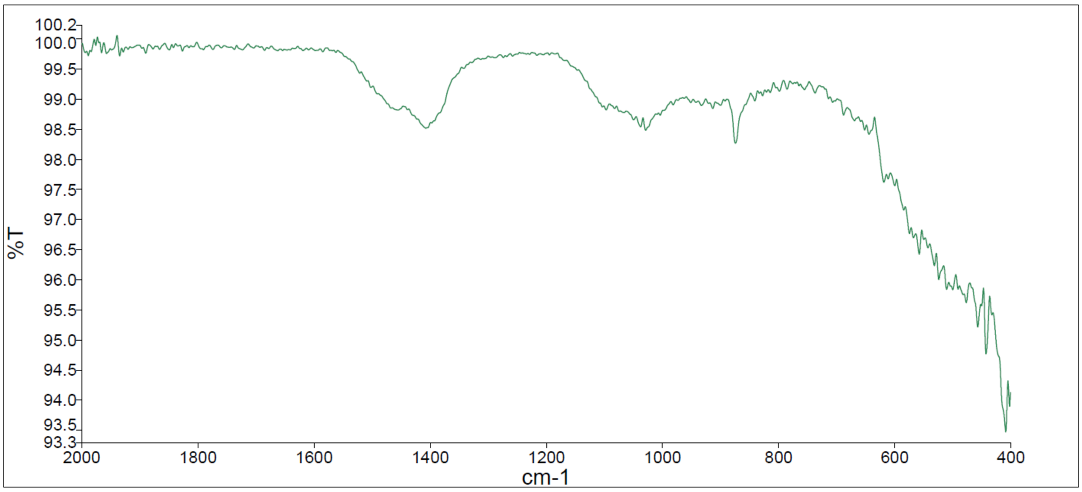

Fig 3: CAC

In figure (3) as for the case of CAC, the FTIR shows intense peak at 1440-1390 cm^{-1} which act as OH bending vibration of alcohol of medium intensity. At 1950-1890 cm^{-1} there is C-H bending vibration acts as an aromatic compound. At 1300-1250 cm^{-1} there is C=C stretching vibration of alkene and also the C-H bending peaks at 900-830 cm.

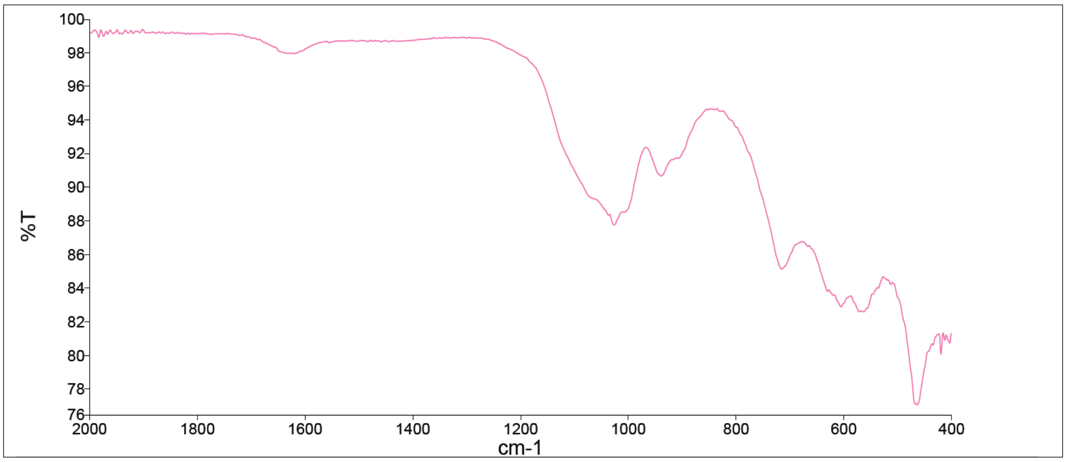

Fig 4: BNC

As given in figure (4) as for the case of BNC, the FTIR shows the intensity of BNC at 1930-1850 cm^{-1} of OH stretching vibration of maximum intensity. C=C shows an intense stretching vibration peak at 1100-1050 cm^{-1}. C-C bending vibrations shows peak at 960-880 cm^{-1}. Also, the vibration at earlier stage shows the presence of metals in the sample. Fe-O bending vibration shows peak at 790-750 cm^{-1}. Zn-O bending vibration also shows peak at 590-530 cm^{-1} that shows the presence of zinc and iron metal in BNC.

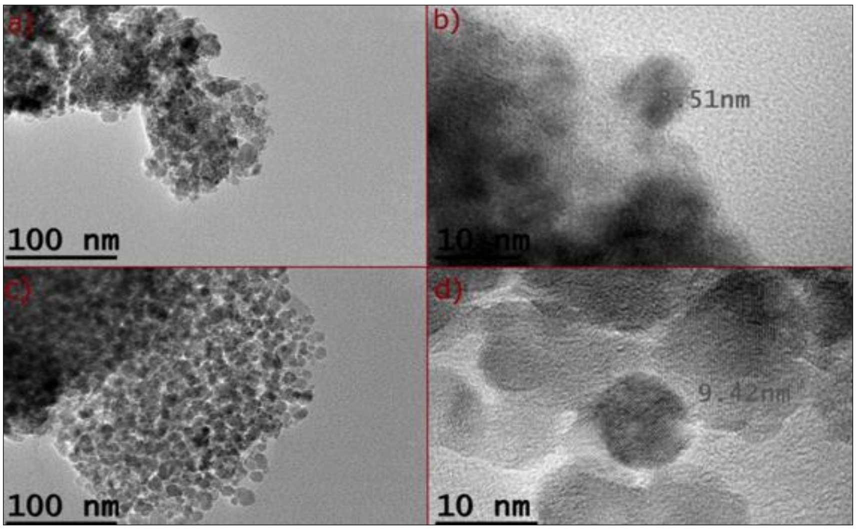

Fig 5: TEM (Transmission electron microscopes)

These images give the detailed information about the internal structure of BNC. As we see in the images, the white lines surrounding the pores are of Zinc while the darkish black portion is of Iron. This shows that how zinc and iron salts are bonded with each other during the synthesis of BNC.

VSM and BET Analysis

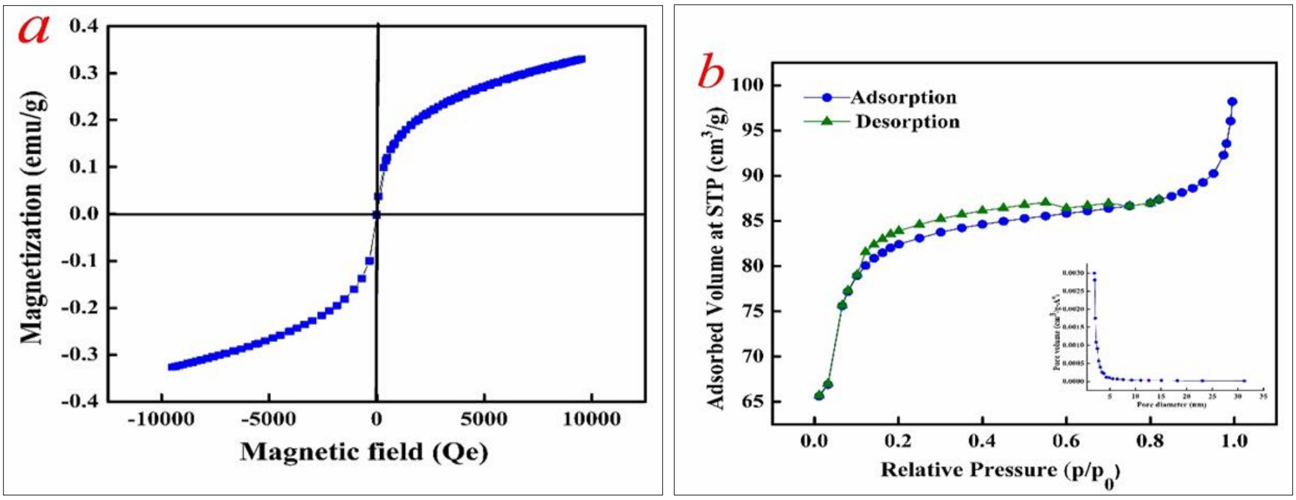

Image (a) gives us the information about magnetism. This graph designates S- like loop which shows the super paramagnetic behavior of our synthesized BNC while Image (b) indicates the higher surface area of our BNC which has a high porosity and good adsorptive capacity which enables to bind the impurities and heavy metals with BNC.

Batch Adsorption Experiment

The adsorption of dye solution was performed using batch adsorption experiments. It was conducted in a set of 500 mL Erlenmeyer flasks containing known amount of adsorbent and 50 mL of methyl orange dye solution with same initial concentration. The flasks were agitated in an incubator shaker at 140 rpm for definite contact time until the equilibrium reached. Then the aqueous phase was separated by centrifugation at 3500 rpm for five minute and then filtered. The equilibrium concentration of dye solution was determined using UV-visible spectrophotometer at 550nm. The percentage removal of dye was calculated using Eq. (1) as follows:

$$\% \text{ Dye removal} = \frac{C_0 - C_t}{C_0} \times 100 \qquad (1)$$

where C0 (mg/L) and Ct (mg/L) are the dye concentrations at initial and any time t, respectively.

The experimental conditions have been investigated and optimized at different dye concentrations (40-100 ppm), adsorbent dosage (100–250 mg), pH of solution (4.0–10.0) and contact time (40-180 minutes). This experiment gives us the study about our BNC that whether it has adsorptive properties is there or not. Therefore, dye solution helps us to study the absorption value of BNC by various parameters at various conditions.

We do experiments and by the use of above formula we calculate different results according to different parameters. By the use of UV- spectroscopy we get absorbance values of both initial and final sample according to the conditions. By the use of these obtained values, we get % removal of dye solution and hence we get the desired result.

We perform different studies according to different parameters and hence get the results. We show the values by the help of graphical representation which helps us to relate the results easier as follows:

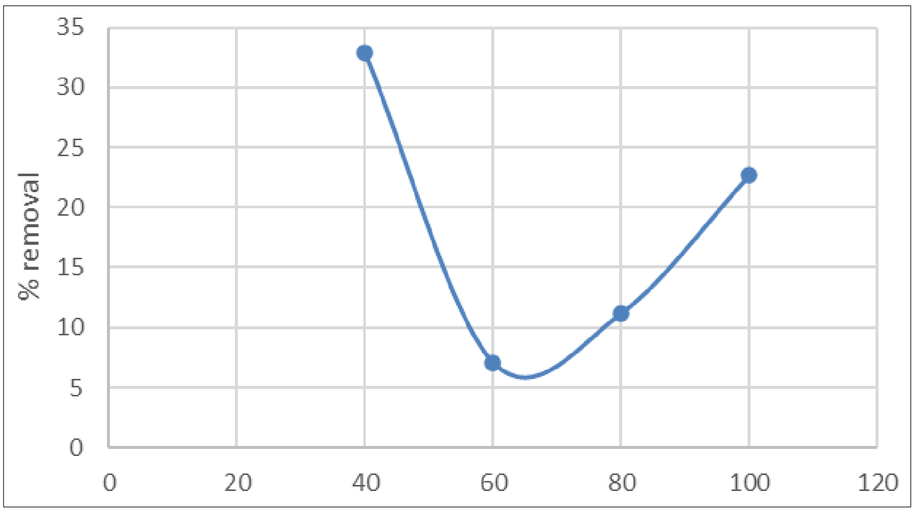

Fig 6: concentration of dye (In ppm)

Effect of Initial Dye Concentration: The influence of concentration of dye solution over the range of 40-100ppm was illustrated in figure (5). The removal percentage decreased from 33.84% to 21.81% with increase in the dye concentration. When the initial concentration increased, more dye molecules sorbed on the surface of BNC sorbent, thus distribution coefficient (Rd) decreased, which indicates that limited numbers of sorption sites are available for the adsorption at higher concentration of adsorbate molecules. This effect can also be explained that active sites required for the adsorption of dye molecules are lacking at higher concentration [10-11].

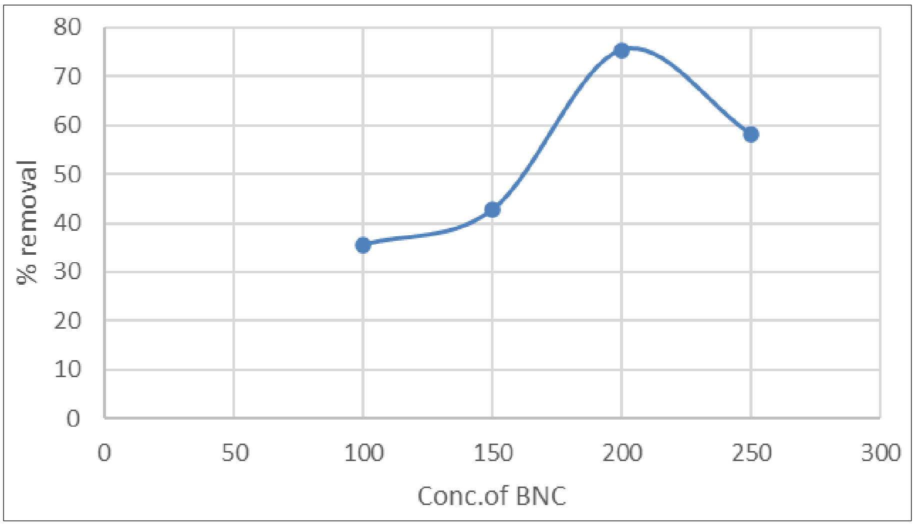

Fig 7: Conc. of BNC

Effect of BNC Dose: The effect of BNC dosage was studied by varying the amount of bio-nanocomposite from 100 to 250 mg at the constant dye concentration (40ppm). It was obvious from figure (6) that the percentage dye removal increased with increase in the amounts of biosorbent and reached a plateau (75.4%) at 40ppm. It was due to the more active sites and greater surface area available for the same number of sorbate molecules. However, there is no significant increase in effective surface area, after 200mg of biosorbent loading because adsorbent molecules grouped together to form cluster [12-13].

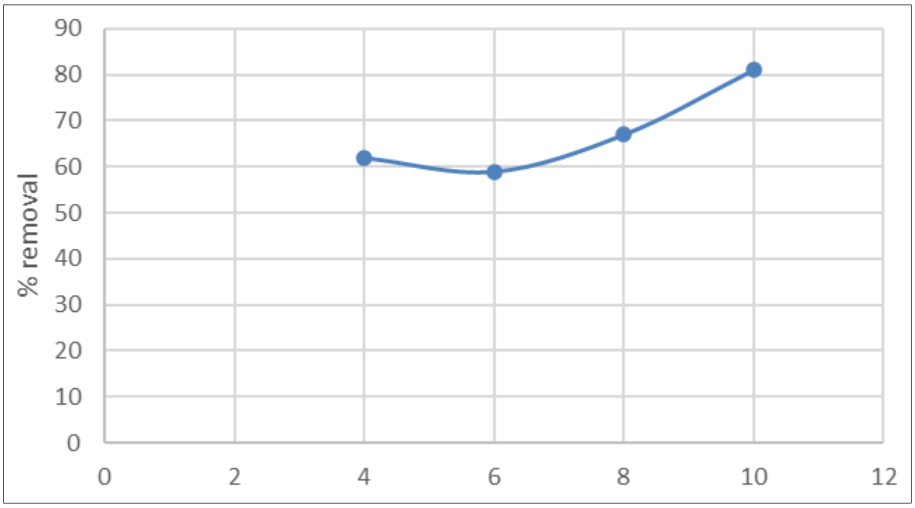

Fig 8: Change in pH

Effect of Solution pH: The pH of the solution is an essential parameter that controls the overall adsorption process. The effect of pH on the adsorption of dye by BNC was studied in between pH 4-10. However, biomaterials are amphoteric in nature and their surface can be positively or negatively charged depending upon pH of solution. Biosorbent adsorbs anions at lower pH due to existence of H+ ions and cations at higher pH due to the presence of OH− ions. It was inferred from figure (7) that removal of dye increased with the pH of solution (4.0-10.0). The maximum removal efficiency (81%) was observed at pH 10.0. At lower pH electrostatic repulsion takes place between positively charged surfaces of biomaterial and dye molecules which does not favour the adsorption onto BNC. The H^+ ions competing for the active sites along with dye which also reduced the sorption performance. While at higher pH (6.0-12.0), biosorbent exterior acquires negative charge which increased the sorption of positively charged dye due to electrostatic force of attraction [14-15]. (E.L. Abd *et al.*, 2009, P.K. Malik *et al.*, 2003)

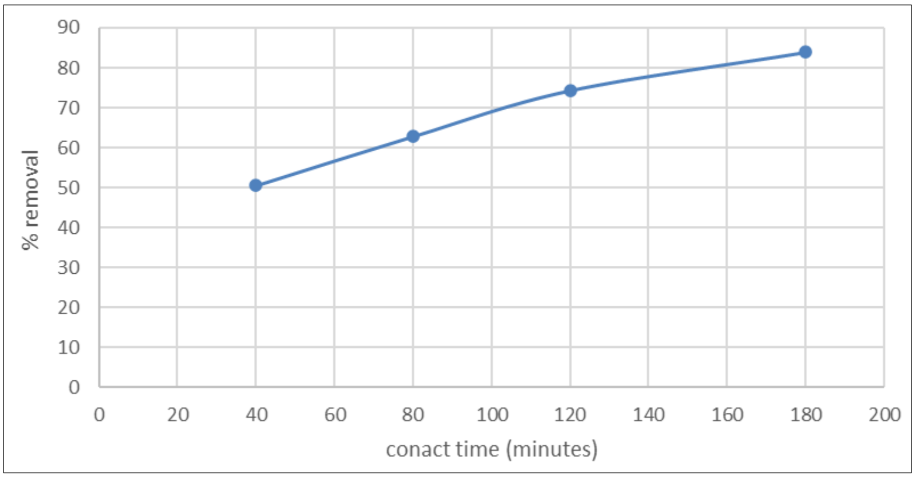

Fig 9: Coenact (Minutes)

Effect of Contact Time - Equilibrium time is the essential factor intended for the treatment of waste water system. The effect of contact time onto dye adsorption was examined at the optimized initial dye concentration (40 ppm), sorbent dosage (200 mg) and pH of solution (10.0). Figure (8) inferred that the percentage adsorption of dye increased from 50.47% to 83.9% as contact time varied from40–180 min. So, based on outcome, 180 min was taken as equilibrium time for the adsorption experiments [16-17].

Conclusion

Traditional wastewater treatment technologies remain ineffective for providing safe water due to increasing demand of water coupled with health guidelines and emerging contaminants. Nanotechnology-based multifunctional and highly efficient processes are providing affordable solutions to wastewater treatments. Nanotechnology has been considered effective in solving water problems related to quality and quantity. Nanomaterials (e.g., carbon nanotubes (CNTs) and dendrimers) are contributing to the development of more efficient treatment processes among the advanced water systems.

Herein we report the synthesis of BNC with the help of Tulsi leaves and synthesis of nano material using manganese chloride, zinc chloride and iron chloride salts. The study of FTIR confirmed the synthesis of BNC with the help of these salts. To check the magnetic properties of BNC we use bar magnet from which we observe that the particle of BNC gets attached to the surface of magnet due to its property of magnetism. Thus we conclude that the magnetic behavior of BNC is due to the unpaired electrons in the outermost shell. In case of application part, we use methyl orange dye solution for checking the adsorption quality of BNC. We use different parameters such as effect of initial concentration of dye, effect of BNC concentration, effect of pH and contact time. Then we observe the nature of BNC by checking the percentage purity of the dye solution before and after adding the BNC by the help of absorbance values of dye solution which is calculated by UV spectroscopy.

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