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Remediation of Thermal Power Plant Effluent with Chitosan and Chitosan Trisodium Polyphosphate nanoparticles

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ABSTRACT

Because water is necessary for life to exist on Earth, it is equally important to clean it of pollution. Due to its use in industry, industrialization has put tremendous pressure on water utilization. Industrial effluents are produced in enormous quantities as a result of increased output. For the sustainable development of companies and the environment, these industrial effluents must be treated in a precise and economical manner. To lessen the toxicity of wastewater effluents and to make their use sustainable, a variety of electrochemical, cutting-edge oxidation and valorization techniques have been used. But not all sectors can afford to use these methods. With the development of environmentally friendly nanomaterials, industry can spend less money on mitigating harmful pollutants thanks to nanotechnology. Nanomaterials are gaining attention due to their enhanced physical, chemical and mechanical properties. Several investigations on inexpensive adsorbents for removing heavy metals from natural resources have recently been conducted. The present study employed waste from the shrimp processing industry as an example of one of these types. Chitosan is a biodegradable and biocompatible polymer that is created by deacetylating chitin and is a low-cost adsorbent. The ability of chitosan and chitosan TPP nanoparticles to adsorb heavy metals from thermal power station effluents was tested in the current study. Thermal power plant effluents were collected and samples were analyzed to assess major ionic constituents, trace metal pollution (Chromium, Lead, Zinc, Iron, and Cobalt). The ability to remove the five heavy metals such as chromium, lead, zinc, cobalt, and iron from thermal effluents was demonstrated by both chitosan and chitosan TPP micro particles. When compared to chitosan alone, chitosan TPP nanoparticles demonstrated high effectiveness in the adsorption of heavy metals. Our findings indicated that chitosan and chitosan TPP nanoparticles have a significant capacity for adsorbing certain metal ions and that the adsorption process is concentration driven. The current study also gives economical solution for wastewater treatments discarding by small scale industries.

Key words: Nanotechnology, Coagulation-adsorption, Chitosan, Chitosan TPP nanoparticles, Thermal power plant effluent, Shrimp waste management, Heavy metals.

INTRODUCTION

A significant issue in the worldwide context is water pollution brought on by the discharge of untreated industrial effluents into water bodies (Mathuthu et al., 1997). Both wealthy and developing nations struggle with the issue of water contamination. Water pollution is caused by human activities that introduce different types of garbage or pollutants into a water body. One of Andhra Pradesh's nine coastal districts, Nellore is located in the state's southeast.

There are numerous large-scale industries in the southern Nellore region, including micro and small businesses, public sector organizations, enormous multinational corporations and large-scale industries. Mica mines and thermal power plants are two of the region's key industries. There is significant hazardous waste creation as a result of industrial operations. Textile, chemicals, pharmaceuticals, pesticides, paint and dye, fertilizers, mica, paper manufacture, inorganic chemicals, power plants and general engineering industries are among the biggest hazardous waste-producing businesses in Nellore. Heavy metals, cyanides, pesticides, complex aromatic compounds (like PCBs) and other chemicals that are poisonous, combustible, reactive, corrosive, or have explosive properties harm the environment are present in hazardous wastes from the industrial sectors indicated above (Kumar et al., 2000).

Heavy metals and effluent from thermal power plant businesses are released into the environment directly or indirectly, particularly in developing nations. They tend to accumulate in living organisms because of their toxicity and lack of biodegradability. As a result, they contribute too many illnesses and disorders. Trace amounts of heavy metals (Cr, Fe, Pb, Zn, Co, etc.) in water have a significant impact on the ecology of the water and consequently, on human servility. Water quality is deteriorated by the contamination of certain heavy metals, which results in changes to water's pH, EC, TDS and other characteristics. The severe degradation of the aquatic environment has an impact on fishing resources and their habitats by altering natural processes and natural resource communities. To safeguard the environment, it is crucial to pinpoint the problems and find solutions.

Heavy metal pollution in aquatic environments has unavoidably increased as a result of the massive rise in heavy metal use over the past few decades. Heavy metal concentrations are higher in the effluents from thermal power plants, which can contaminate water when released into the environment. The toxic heavy metals zinc, copper, nickel, mercury, cadmium, lead and chromium are of particular concern when treating industrial wastewaters. Although they are crucial to the growth and development of any nation, thermal power plants have both direct and indirect negative effects on the environment. These industries have expanded steadily and are now sources of pollution. Due to the usage of chemicals containing hazardous components and heavy metal ions during rapid industrialization and widespread urbanization, our environment has become more contaminated (Brown et al., 1996). The lack of wastewater treatment facilities in the majority of Indian cities and industry is concerning.

Domestic and industrial sewage are dumped into receiving water bodies without being treated because wastewater treatment is not given the required priority it requires. Because industrial effluents contain heavy metal ions that are released into the environment, metallic pollution in particular poses a risk to humanity. As a result, river pollution increases, aquatic life declines, and plants and animals consume polluted water, which eventually enters human bodies and causes health issues. Heavy metals are highly harmful at low concentrations and can build up in living things, resulting in a variety of ailments and diseases (Gotoh et al. 2004). This is because they are soluble in water as ions or in compound forms and can be easily absorbed by living things. Due to their widespread use, the effective removal of harmful metal ions from wastewater is a significant and actively researched topic, and numerous methods have been created in this area over time (Deans and Dixon, 1992).

Filtration, chemical precipitation, ion exchange, adsorption, electro deposition, and membrane systems are among the most crucial of these techniques (Kishku et al., 2001). All of these methods have intrinsic benefits and limitations. Both filtration and chemical precipitate ion may swiftly remove significant amounts of metal ions at minimal expense, but neither can get rid of tiny amounts. At extremely low metal ion concentrations, adsorption is likewise useless. Metal concentrations can be lowered through ion exchange to a few parts per million (Nivruti et al., 2013). Studies on polymers that bind metal ions have grown dramatically in recent years. The potential of biopolymers to reduce transit ion metal-ion concentration to parts per billion concentrations, their availability, and their environmental safety are only a few of the factors that make them appealing to industry. Cellulose, alginates, carrageenan, lignins, proteins, chitin, and chitin derivatives are a few examples of these materials. Biopolymers are also appealing because they contain a variety of functional groups, such as hydroxyls and amines, to which metal ions can attach through chemical or physical adsorption (Deans and Dixon, 1992). Chelation ion exchange, used as a final step after the majority of the metal ions have been removed, can improve the efficiency of metal removal. It is impracticable to use metals used for chelation ion exchange to remove significant amounts of heavy metals from water because of their higher associated production costs.

Adsorption has emerged as one of the alternative heavy metal-laden waste water treatment methods. A substance is essentially moved from the liquid phase to the surface of a solid by the mass transfer process known as adsorption, where it is then bonded by physical and chemical reactions (Kurniawan et al., 2006). For the adsorption of dyes and heavy metals in wastewater treatment, chitosan composites have been studied (Ravi Kumar, 2000). In order to determine how chitosan and Chitosan TPP nanoparticles affect the remediation of thermal power plant effluents, this study was conducted.

The objectives of the study are as follows

1) Collection of thermal power plant effluents
2) Treatment of effluent samples with chitosan and chitosan TPP nanoparticles
3) Determination of removal efficiency of heavy metal concentration

MATERIALS AND METHODS

Sampling of thermal power plant effluents

The study was carried out at Nellore urban industrial area which is one of the most rapidly developing and polluted industrial area of Nellore. Samples were collected in 100 ml Plastic bottles. The samples were collected from January 2018 to March 2018. The thermal power plant effluents were collected for heavy metal analysis from ten different stations (Table-1) of the surrounding industrial aquatic environment directly from the outlet of the factory linked to canal. The sample container bottles were thoroughly cleaned with hydrochloric acid, cleaned with tap water to render free of acid, washed with distilled water twice, again rinsed with the water sample to be collected and then filled up the bottles and immediately transported to the laboratory. Effluent samples were then filtered through filter paper (Whatman No. 42) to remove undesirable solid and suspended materials. Collected water samples were analyzed for heavy metals (Chandra Sekar, 2016).

Table-1: Sampling site with sampling code in detail

S.No	Sample ID	Location
01	E1	Muthukur
02	E2	Krishnapatnam
03	E3	Nelatur
04	E4	Painapuram
05	E5	Sivaramapuram
06	E6	Eruru
07	E7	Momidi
08	E8	Ankulapaturu
09	E9	Thumminapatnam
10	E10	Sivaramapuram

Treatment of water samples with chitosan and chitosan nano particles

In the trials, chitosan and chitosan TPP nanoparticles were used to coagulate a sample of wastewater from a thermal power plant using a standard jar test device. Chitosan and chitosan nanoparticle concentrations of 5, 10, 15, and 20 mg/100 ml were applied to effluent samples. After shaking the beakers, 300 rpm flash mixing started right away and continued for 10 minutes. After then, the mixing speed was lowered to 30 rpm and maintained there for 20 minutes. Finally, a 30-minute quiet settling period was permitted. A sample of the supernatant was tested for the presence of heavy metals after the settling period (Maram et al., 2022). At an ambient temperature of 26 to 30 °C, all experiments were run.

Analysis of Heavy metals

Digestion of Samples

All of the wastewater samples underwent sample digestion for heavy metal analysis both before and after treatment with chitosan and chitosan TPP nanoparticles. It was decided to filter a 100 ml sample of effluent with Whattmann filter paper. After that, a 100 ml beaker containing the water sample was placed on a hot plate and set to 100°C for evaporation. 10 ml of 4N HNO_3 are added to the sample's precipitate after it has completely evaporated, and the mixture is then thoroughly stirred. For complete sample evaporation, the aforementioned solution was heated to 40°C. The precipitate will stay at the bottom of the beaker after complete evaporation. The above precipitate is made-up with 1N HCl to 100 ml and store in plastic bottles for the analysis of heavy metals by using Atomic Absorption Spectrophotometer (AAS),(Aremu et al., 2007).

Determination of heavy metals in effluents

Using an Atomic Absorption Spectrophotometer (AAS), several heavy metals (chromium, lead, iron, zinc, and cobalt) were identified in water samples (Varian Spectra AA55B, Australia). The heavy metal content of waste water samples was directly determined using the filtered water sample. Plotting the absorbance measurement on the Y-axis against the concentration of each standard metal solution on the X-axis resulted in the creation of a standard line. Then, by plotting the AAS reading on the standard line, the metal concentration in the relevant water samples was determined (APHA 2002).

Data Analysis

Statistical analysis of the data generated out of the chemical analysis of water samples was done. The SPSS 25 and Microsoft Office Excel software were used for data analysis and presentation.

RESULTS AND DISCUSSION

Adsorption studies on Chromium

This study demonstrated the effective use of synthetic chitosan and chitosan TPP nanoparticles in the reductive removal of harmful chromium ions from thermal power plant effluents. Prior to treatment, all effluent samples were found to have more chromium than 70 ppm. Figure-1 displays the results of treating these materials with various doses of chitosan and chitosan nanoparticles. Following treatment, the concentration of chromium in several water samples varied from 1.703 to 44.316 ppm. It was discovered that the chromium adsorption increased as chitosan and chitosan nanoparticle concentration increased. With a 20 mg dosage for both chitosan and chitosan nanoparticles, the decrease in chromium content was significant.

With chitosan the concentration of chromium was found to decrease up to 6.000 ppm with sample E10 where as with chitosan nano particles it was 1.703 ppm for the sample E7.

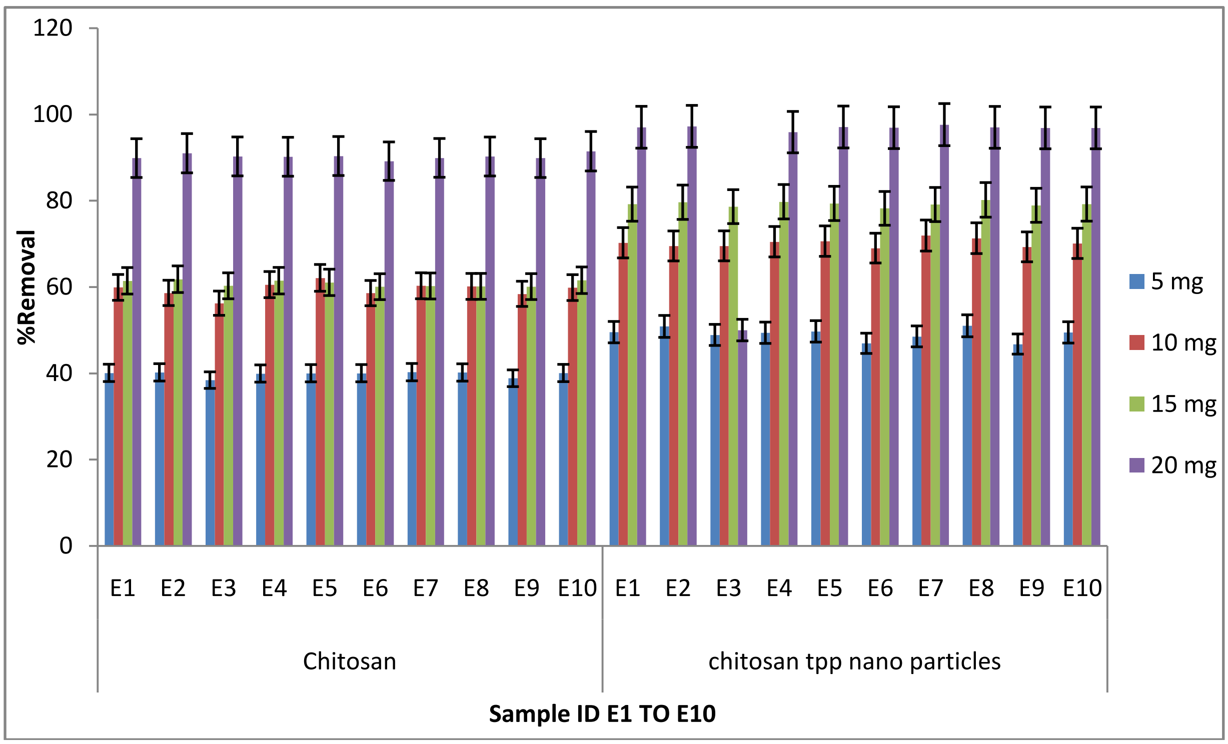

Figure-1: Chromium (Cr) removal effecieicency of Chitosan and Chitosan TPP nanoparticles from thermal power plant effluents.

When compared to chitosan, Chitosan TPP nanoparticles demonstrated high efficiency. The significant differences in chromium adsorption between chitosan and chitosan TPP micro particles over concentrations of 5, 10, 15, and 20 were discovered using a two-way ANOVA. To compare the significance of means, Bonferroni Post-T replicates by row were used. Using the statistical programme Graph Pad Prism V5, $P<0.05$ is the threshold at which a difference is deemed significant results were depicted in Figure-2.

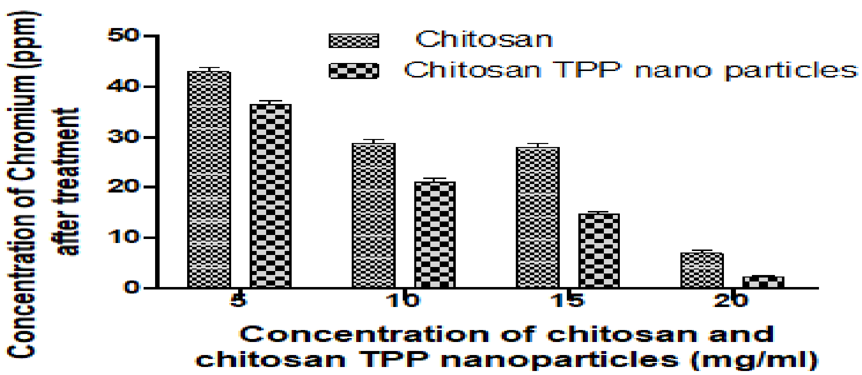

Figure-2: Effect of Chitosan and Chitosan TPP nanoparticles dosage on adsorption of Chromium (ppm) from thermal power plant effluents

Because of its mutagenic and carcinogenic characteristics, hexavalent chromium is widely recognized as a group "A" human carcinogen. It is listed among the most dangerous compounds because it has an impact on both aquatic and terrestrial life. Additionally, it has been documented that heavily cultivated pulse crops suffer from reduced seed germination and significant mitotic process disruption caused by excessive hexavalent chromium intake by plants (Altaf et al., 2008). The majority of companies use chromium compounds in an effort to raise human living conditions, yet untreated chemical discharge into the environment has the opposite effect of what was intended. The greatest contributors to chromium pollution are thermal power stations, followed by the leather tanning industries. Despite, a lot of research work published on natural adsorbents for pollutants uptake from contaminated water, there is yet little literature containing a full study of removal of Cr(VI) by using chitosan and its cross-linked derivatives (Manfe et al., 2012).

Adsorption studies on Lead

The adsorption of lead (II) from thermal power plant effluents onto chitosan and chitosan TPP nanoparticles was examined in the current work. Lead concentrations greater than 8 mg/L were reported in all wastewater samples. Lead content was lowered to 0.213 ppm after treatment with chitosan and chitosan TPP nanoparticles (Figure-3). It was discovered that the lead adsorption increased as chitosan and chitosan nanoparticle concentration rose. With a 20 mg dosage for chitosan and chitosan nanoparticles, the reduction in lead content was significant. Lead content was observed to decrease with chitosan up to 1.007 ppm with sample E4, however it was only 0.213 ppm with chitosan nanoparticles for sample E10.

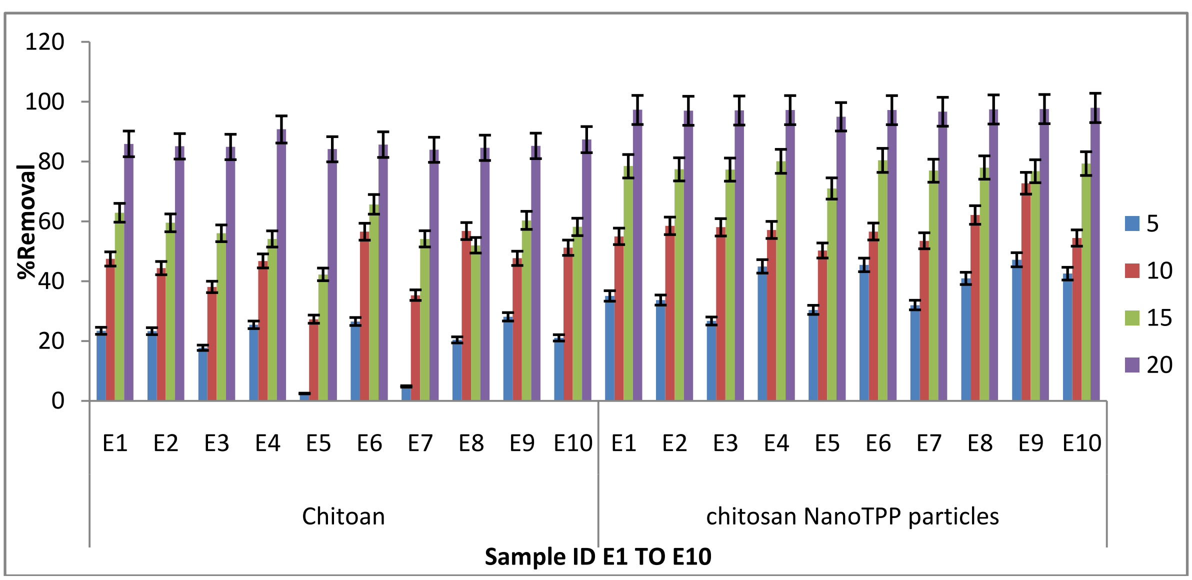

Figure-3: Lead (Pb) removal effecieicency of Chitosan and Chitosan TPP nanoparticles from thermal power plant effluents.

Chitosan TPP nanoparticles showed high efficiency in the removal of lead from effluents with compared to chitosan. Two-way ANOVA was employed to find the significant differences in adsprption of lead over a concentration of 5, 10, 15 and 20 between chitosan and chitosan TPP nano particles. Bonferroni Post-T replicates by row were performed to compare the significance of means. The considered significant level is at $P<0.05$ by using the statistical software package GraphPad Prism V5 (Figure-4).

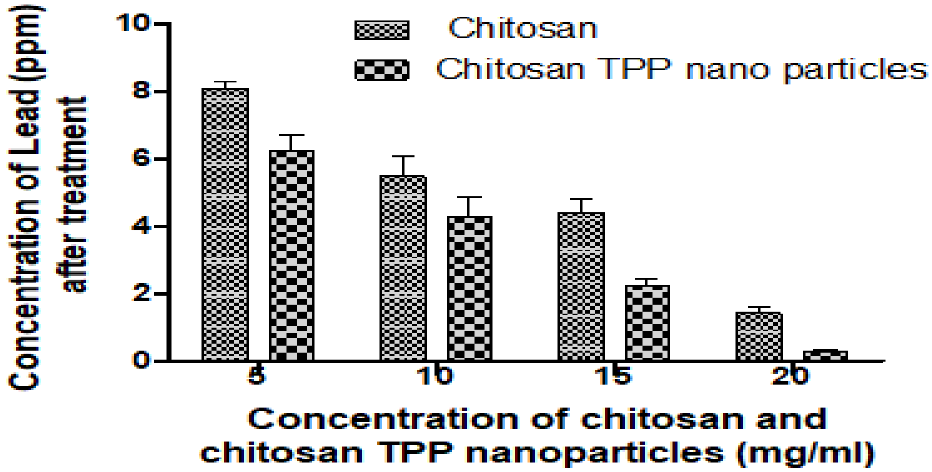

Figure-4: Effect of Chitosan and Chitosan TPP nanoparticles dosage on adsorption of lead (ppm) in thermal power plant effluents

Yan and Bai (2010) studied the adsorption capacity of lead on to chitosan hydrogels beads and reported that amine groups in chitosan were found to play the major role in the adsorption of lead ions or humic acids, and when these two were simultaneously adsorbed their removal was significantly lower.

Adsorption studies on Zinc

Zinc levels in the wastewater samples taken from the various industrial areas ranged from 21.460 to 16.150 ppm (Figure-5). The point E6 had the highest concentration (21.460 ppm), whereas the point E1 had the lowest value (16.150 mg/L). Zinc concentration decreased after treatment with chitosan and chitosan nanoparticles to 8.058 and 0.548 ppm, respectively. For chitosan, zinc concentration decreased to 2 ppm with samples E1 and E10, while it was 0.548 ppm for sample E1.

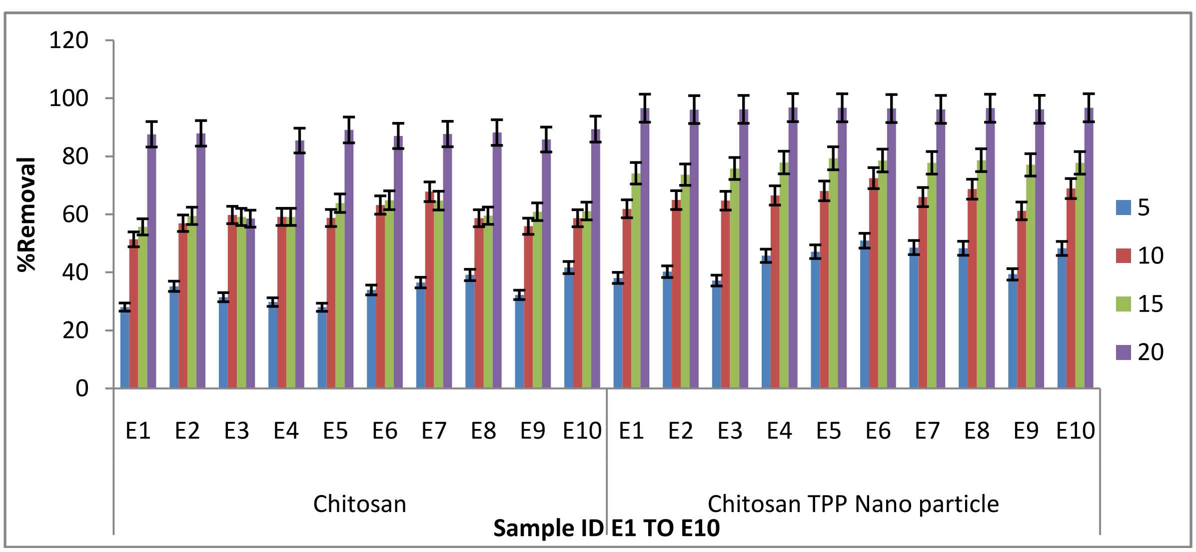

Figure-5: Zinc (Zn) removal effecieicency of Chitosan and Chitosan TPP nanoparticles from thermal power plant effluents.

The maximum allowable amount of zinc in irrigation water is 2.00 mg/L, according to Ayers and Westcot (1985). The Zn concentration of the samples is greater than the recommended value for aquaculture since all effluent samples treated with chitosan and chitosan TPP nanoparticles were determined to be above the maximum allowable limits that were suitable for irrigation in respect of Zn. The water is therefore dangerous for aquatic life and unfit for aquaculture. Chitosan and Chitosan TPP nano particles were compared for their ability to spread zinc over concentrations of 5, 10, 15, and 20 using a two-way ANOVA (treated). To compare the significance of means, Bonferroni Post-T replicates by row were used.

The considered significant level is at $P<0.05$ by using the statistical software package GraphPad Prism V5 (Figure-6).

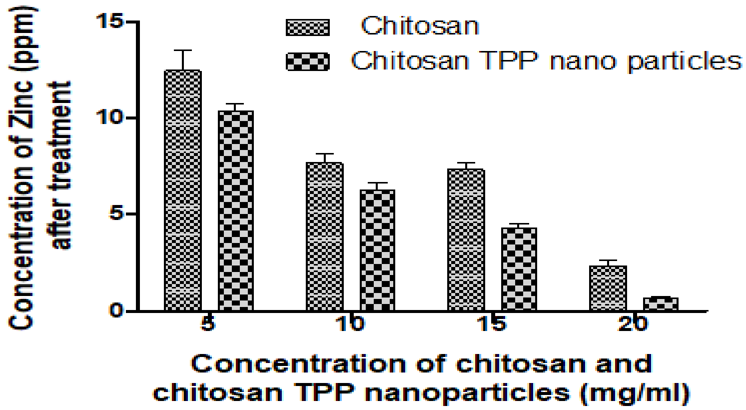

Figure-6: Effect of Chitosan and Chitosan TPP nanoparticles dosage on adsorption of Zinc (ppm) in thermal power plant effluents

The use of activated carbon for adsorption is restricted by its expensive cost. For the removal of heavy metals, numerous types of inexpensive adsorbents have been created and tested. Chitosan was investigated by Karthikeyen et al. (2004) for the elimination of Zn (II). They discovered that for chitosan to remove zinc (II) as effectively as possible, an ideal contact time of six minutes was needed. The adsorption mechanism is further influenced by the adsorbent's particle size, the medium's pH, and the presence of additional anions such chlorides and nitrates. The ideal pH was discovered to be 70, and the equilibrium values fit the Langmuir isotherm nicely. The feasibility of precipitating the heavy metal ions Mn(II) and Zn(II) using water-soluble chitosan was investigated by Guan et al. in 2009. FT-IR analysis was also carried out between chitosan and metal ion. The optimum pH was found in the range from 5 to 9, there were three stages for different actions: precipitation of metal hydroxide and co precipitation of metal hydroxide and chitosan–metal complex, chelation of chitosan for metal ion. The selective chelation of chitosan for Mn (II) and Zn (II) mixture solution was also studied.

Adsorption studies on Iron

The adsorption of iron from thermal power plant effluents on to chitosan and chitosan TPP nanoparticles was examined in the current study and is shown in Figure-7. The concentration of iron was found to be greater than 20 ppm in all effluent samples. The range of iron concentration after treatment with chitosan and chitosan TPP nanoparticles is 14.097 to 0.498 ppm. It was discovered that when chitosan and chitosan nanoparticle concentration rose, so did the iron adsorption. With a 20 mg concentration for both chitosan and chitosan nanoparticles, the reduction in iron concentration was significant. Iron concentration was shown to decrease with chitosan up to 2.149 ppm with sample E4, but it decreased to 0.498 ppm with chitosan nanoparticles for sample E8.

In order to remove Fe(III) from aqueous solutions, Gandhi et al. (2014) created a series of modified chitosan beads (CB). However, the protonated (PCB), carboxylated (CCB), and grafted CB (GCB) modified versions of chitosan beads did not have a high enough adsorption capacity (7.042, 9.346, and 14.286 mg/g, respectively). The significant differences in iron absorption between chitosan and chitosan TPP nanoparticles over concentrations of 5, 10, 15, and 20 were discovered using a two-way ANOVA. To compare the significance of means, Bonferroni Post-T replicates by row were used. Using the statistical programme Graph Pad Prism V5, P0.05 is the threshold at which a difference is deemed significant.

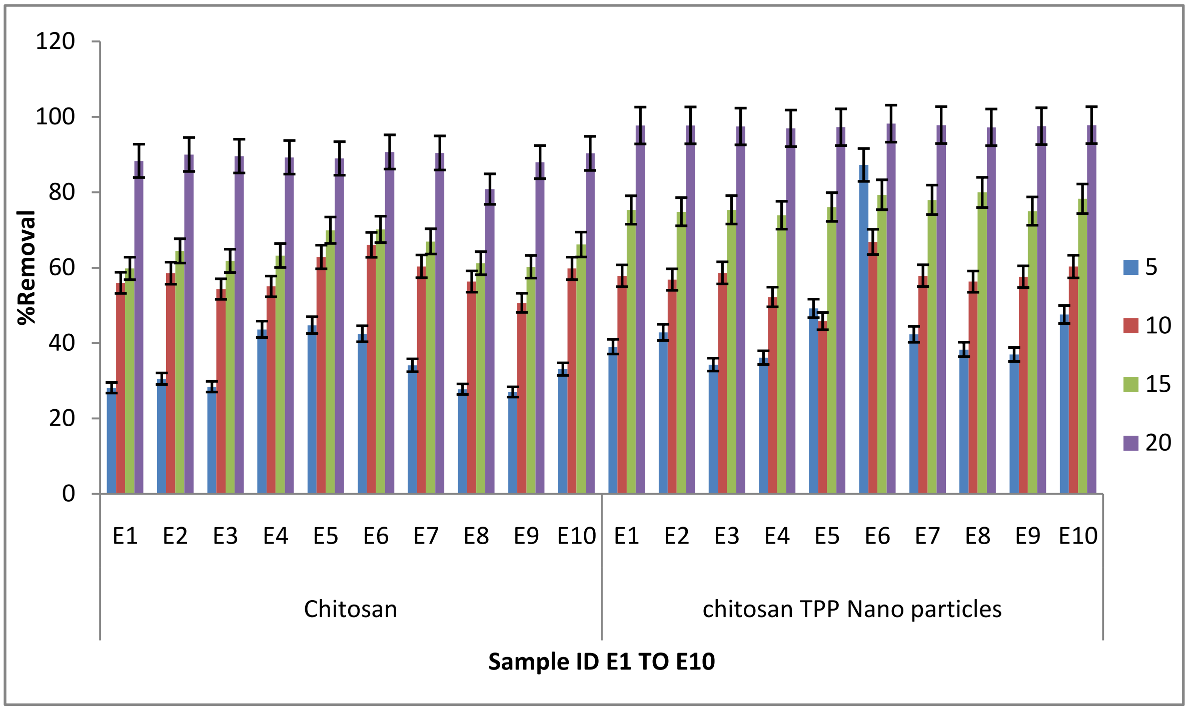

Figure-7: Iron (Fe) removal effecieicency of Chitosan and Chitosan TPP nanoparticles from thermal power plant effluents.

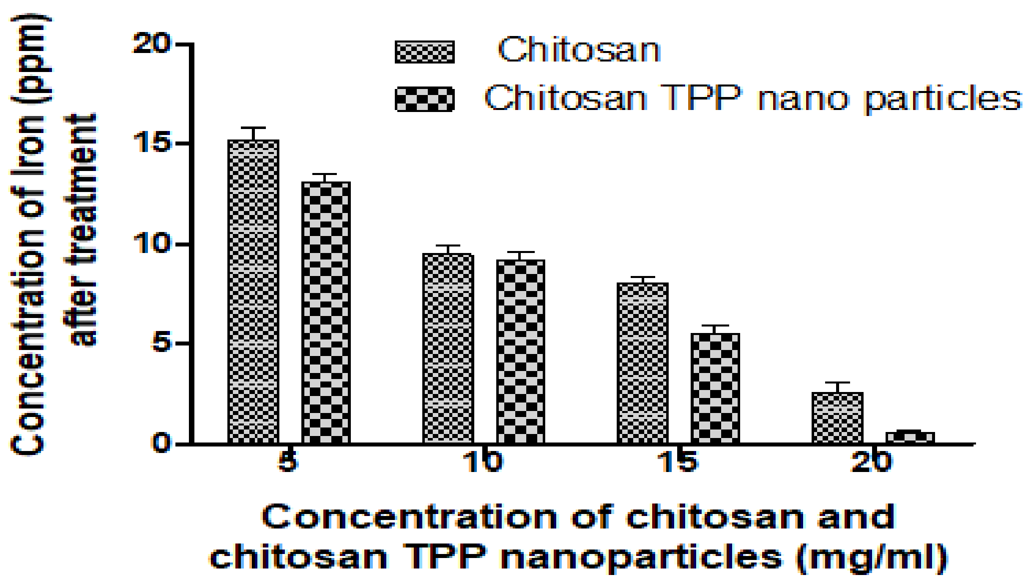

Figure-8: Effect of Chitosan and Chitosan TPP nanoparticles dosage on adsorption of Iron (ppm) in thermal power plant effluents

Adsorption studies on Cobalt

Cobalt levels in the wastewater samples taken from the various industrial areas ranged from 15.461 to 10.081 ppm. (Figure-9). At point E3, the concentration was highest (15.46 ppm), while at point E5, the concentration was lowest (10.081 ppm). Cobalt concentration ranged from 10.001 to 0.388 ppm after treatment with chitosan and chitosan nanoparticles. For chitosan, cobalt concentration was observed to drop up to 1.004 ppm with sample E1, whereas with chitosan nanoparticles, it was 0.388 ppm with sample E7.

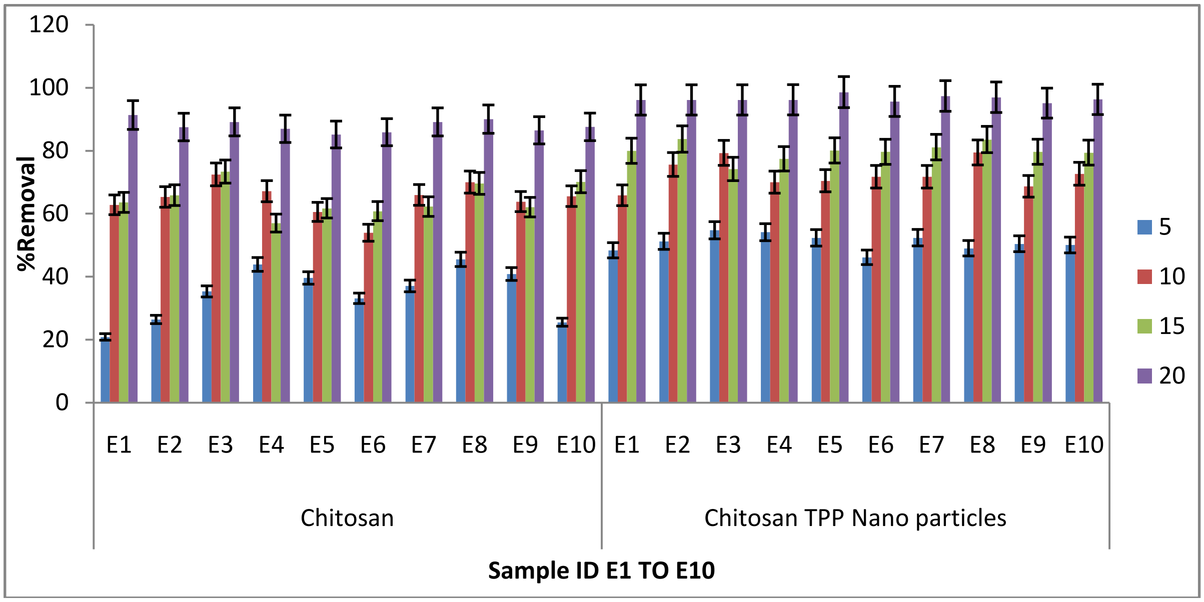

Figure-9: Cobalt (Co) removal effecieicency of Chitosan and Chitosan TPP nanoparticles from thermal power plant effluents.

The significant differences in iron absorption between chitosan and chitosan TPP nanoparticles over concentrations of 5, 10, 15, and 20 were discovered using a two-way ANOVA. To compare the significance of means, Bonferroni Post-T replicates by row were used. Using the statistical programme Graph Pad Prism V5, P0.05 is the threshold at which a difference is deemed significant.

Repo et al. (2013) studied the elimination of Co(II) using chitosan that had been EDTA-modified. The produced material has a specific surface area of 0.71 m2/g and a total pore volume of 1.8 103 cm3/g (610 average pore size). This adsorbent tested for Co(II) removal and showed Qm equal to 1.35 mmol/g (Langmuir, Sips equations) (Repo et al., 2010). Song et al., 2014 prepared a novel xanthate carboxy methyl grafted chitosan derivative for removal of Cu(II) and Ni(II) from aqueous solutions. The effect of pH was tested in the range of 2.0–7.0 and Qm was calculated using Langmuir and Freundlich models to be 174.2 mg/ml and 128.4 mg/ml for Cu(II) and Ni(II), respectively.

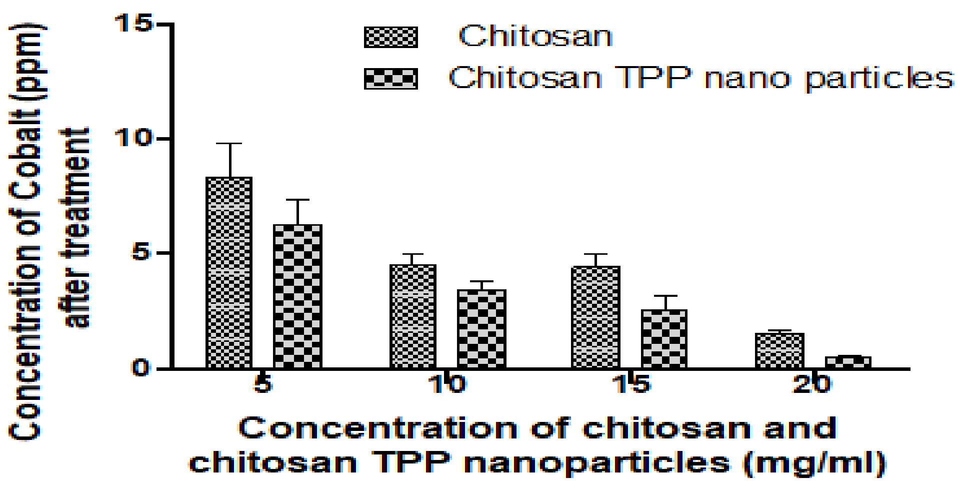

Figure-10: Effect of Chitosan and Chitosan TPP nanoparticles dosage on adsorption of Cobalt (ppm) in thermal power plant effluents

Numerous works by Muzzarelli et al. (2014) describe the chelation of various ions with chitosan derivatives. In order to remove and measure Cd(II) from waterways, Arvand et al. (2013) created a modified 3,4-dimethoxybenzaldehyde chitosan derivative (Chi/DMB). On the other hand, another grafted chitosan derivative was used to remove a group of ions (Cu(II), Co(II), Zn(II), Hg(II), and Pb(II)) (Kandile and Nasr, 2012). The interaction of chitosan with 4,4′-

diformyl—diphenoxyethane served as the basis for the modification process. The highest absorption was demonstrated at pH 5.0, and the predicted adsorption capacities for Cu(II), Co(II), Zn(II), Hg(II), and Pb(II) were 12, 8, 12, 56, and 50 mg/g, respectively.

CONCLUSION

The vast volume of effluents that are released as waste water into the nearby water bodies as a result of rapid industrialization have a variety of negative effects on the ecosystem. Due to its negative effects on environmental health and safety, water pollution brought on by thermal power plant effluent discharges has become a concerning occurrence. Precipitation and coagulation, ion exchange, electro dialysis, membrane filtration, flotation, reverse osmosis, and adsorption are just a few of the treatment methods that have been utilized to remove heavy metals from wastewater. The majority of these processes have substantial costs.

Several investigations on inexpensive adsorbents for removing heavy metals from natural resources have recently been conducted. The present study employed waste from the shrimp processing industry as an example of one of these types. Chitosan is a biodegradable and biocompatible polymer that is created by deacetylating chitin and is a low-cost adsorbent. The ability of chitosan and chitosan TPP nanoparticles to adsorb heavy metals from thermal power station effluents was tested in the current study. Thermal power plant effluents were collected, and samples were analysed to assess major ionic constituents, trace metal pollution (Chromium, Lead, Zinc, Iron, and Cobalt). The ability to remove the five heavy metals such as chromium, lead, zinc, cobalt, and iron from thermal effluents was demonstrated by both chitosan and chitosan TPP micro particles. When compared to chitosan alone, chitosan TPP anno particles demonstrated high effectiveness in the adsorption of heavy metals. Our findings indicated that chitosan and chitosan TPP nanoparticles have a significant capacity for adsorbing certain metal ions and that the adsorption process is concentration driven.

To ascertain the independent variables' and their interactions' statistical significance, an ANOVA was utilised, along with a level of 0.05 (95% confidence). At 95% confidence intervals, an ANOVA revealed that all effects were statistically significant (P 0.05). As a more recent method for remediating heavy metals from thermal effluents, this work demonstrated that chitosan and chitosan TPP nanoparticles were effective for the reductive elimination of ecologically toxic and hazardous metal ions. Chitosan as a result of its bioavailability would be economically useful for the treatment of waste water containing heavy metals.

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