

“Sustainability Criteria for Accessing Nanotechnology Applicability In Karnataka Milk Factory (Dairy), Wastewater Treatment”

Ahmed Parvez Nagarboudi¹, Nisarga Chavan², Abusafiyan³, Arif Ahmed Khan⁴

1. Department Of Civil Engineering, Secab I E T, Vijiyapur, Karnataka, India

2. Department Of Civil Engineering, Secab I E T, Vijiyapur, Karnataka, India

3. Department Of Civil Engineering, Secab I E T, Vijiyapur, Karnataka, India

4. Department Of Civil Engineering, Secab I E T, Vijiyapur, Karnataka, India

ABSTRACT: Sustainable nanotechnology has made substantial contributions in providing contaminant-free water to humanity. Nanomaterials typically have high reactivity and a high degree of functionalization, large specific surface area, size-dependent properties etc., which makes them suitable for applications in wastewater treatment and for water purification. In the last decade, nanotechnology entered the policy arena as a technology that is presumably well known promising candidate for solving important issues such as ensuring the quality and quantity of potable water for the world society in the 21st century. Nanoparticles have a great potential to be used in waste water treatment. Its unique characteristic of having high surface area can be used efficiently for removing toxic metal ions, disease causing microbes, organic and inorganic solutes from water. Various classes of nanomaterials are also proved to be efficient for water treatment like metal-containing nanoparticles, carbonaceous nanomaterials, zeolites and dendrimers.

Water use results in a decrease in water quality, and serious environmental deterioration results from directly returning used water to the environment. Various physical, chemical and biological treatment processes are used for wastewater treatment. Nanotechnology has been extensively studied by researchers as it offers potential advantages like low cost, reuse and highly efficient in removing and recovering the pollutants. Nanotechnology is also being looked upon to provide an economical, convenient and ecofriendly means of wastewater remediation. Different types of nanoparticles such as nanosized metals, metal oxides, zerovalent ions, Nano filtration membranes have proven effective in detection, removal and/or destruction of contaminants. Chitosan is a polysaccharide prepared by the de-Nacetylation of chitin, which is the main constituent of the shells of crustaceans. Chitosan is a biodegradable cationic polymer that may be a potential substitute for aluminum salts in water treatment systems. In this study, we have compared the coagulation performances of chitosan alone and of that of chitosan nanoparticles and also for chitosan as the aid for coagulation. The coagulation efficiency is evaluated in terms of coagulant dosage, solution pH, removal of water turbidity and suspended solids.

BACKGROUND: The production of potable water from most raw water sources usually entails the use of a coagulation / flocculation stage to remove turbidity in the form of suspended and colloidal material. This process plays a major role in surface water treatment by reducing turbidity, bacteria, algae, color, organic compounds and clay particles. The presence of suspended particles would clog filters or impair disinfection process, thereby dramatically minimizing the risk of waterborne diseases. With aluminum salts, there is a concern about residuals in the treated water and Alzheimer disease and, whilst iron salts are cheaper options, the cost of any imported chemicals can be a serious problem for developing countries. Thus, in recent years, there has been considerable interest in the development of natural coagulants such as chitosan. By using natural coagulants, considerable savings in chemicals and sludge handling cost may be achieved. In recent years, chitosan and *Moringa Oleifera* have been applied as coagulant in water treatment (Folkard et al., 2000). Chitosan molecule has the ability to interact with bacterial surface and is adsorbed on the surface of the cells and stack on the microbial cell surface and forming impervious layer around the cell, leading to the block of the channels. There are many studies on the removal of turbidity, bacteria, parasite eggs such as *Ascaris* and *Fasciola hepatica* eggs from drinking water by using roughing filters and sand filtration (Tabatabaei et al., 2007; Nouri et al., 2008). In addition, chitosan has been studied for use as a coagulant or flocculant for a wide variety of suspensions including silt in river water to microorganisms. The effective coagulation for turbidity removal was achieved in tap water when using much lower doses of chitosan than would be required for complete charge neutralization of the bentonite. Thus, the objective of this experimental study was to evaluate turbidity and TSS removal by Nano-Chitosan alone and chitosan in conjunction with alum as coagulant aid for turbid waters. This project evaluates the efficiency of Nanochitosan as coagulant as well as chitosan biopolymer as coagulant aid.

MATERIALS AND METHODS: *In this prospective experiment, the water samples are collected in plastic cans from dairy industry and physicochemical tests are conducted and the readings are noted down. Then Chitosan is used to prepare the Nano- Chitosan and then preparation of synthetic turbid water is done, then alum solution is prepared and then experimentation is done. Jar test is done for this experiment. Again the tests are conducted and comparisons of results are done then treatment is finished.*

RESULTS: *The results are effective and comparable and statistical. These results are perfectly examined and perfect clarifications can be achieved.*

CONCLUSION: *It can be observed from results that Nano chitosan has shown better removal efficiency in almost all the parameters. For highly turbid water, alum & chitosan showed the removal efficiency of turbidity of 94.75% and 95.5% whereas Nano-chitosan removed turbidity at 95.95%. And when it was tested as a coagulant aid, chitosan behaved very efficient in removal of turbidity (95.9%) and also this decreased the dosage of alum efficiently. For highly turbid water, alum & chitosan showed the removal efficiency of TSS of 92.8% and 90.64% whereas Nano-chitosan removed TSS at 93.52%. And when it was tested as a coagulant aid, the removal efficiency of TSS was shown 93.52% and also it decreased the dosage of alum efficiently.*

KEYWORDS: *Sustainability, Nanotechnology, Industrial wastewater treatment, Nanoparticle, Nanotechnology, Nanomaterials, Water and wastewater treatment, Water reuse, Wastewater, Water Contaminants, Wastewater Treatment, Sewage, nanotechnology, wastewater treatment, nanomaterials, nanoparticles, nanofiltration, nanoadsorbents.*

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I. INTRODUCTION

The importance of water, in maintaining a healthy as well as a prosperous nation in healthy environment is understood from the existence of the civilization on this globe. Water resources are primarily accustomed satisfying the daily desires of living world in and around them. The stream receives domestic and different wastes frequently.

Waste Water is generated from various sources such as residential areas, commercial/industrial properties, agriculture. Today most of the countries are facing drinking water problems and conditions are very severe especially in developing countries. Waste water containing unwanted substances which adversely affect its quality and thus making it unsuitable for use is termed as wastewater. Composition of wastewater varies widely and depends upon the source from which it is generated. When left untreated these constituents may pose threat to living beings and the environment, which makes it essential to treat wastewater before disposal. Various physical, chemical and biological treatment processes are used for wastewater treatment. Among these methods, currently, nanotechnology has been extensively studied by researchers as it offers potential advantages like low cost, reuse and highly efficient in removing and recovering the pollutants. According to WHO about 80% of all diseases in human beings are caused by water, therefore a regular monitoring of such water bodies is very essential for physicochemical and microbiological analysis to know the suitability of water under use not only to check the outbreak of diseases and occurrence of hazards but also to prevent the water from further deterioration.

Nano-materials are typically defined as materials smaller than 100 nm in at least one dimension. Materials that have one dimension in the nanoscale are layers, such as thin films or surface coatings. Two principle factors cause the properties of nano-materials to differ significantly from other materials: increased surface area and quantum effect. In terms of wastewater treatment, nanotechnology is applicable in detection and removal of various pollutants. Heavy metal pollution poses as a serious threat to environment because it is toxic to living organisms, including humans, and not biodegradable. Several methods are employed to ensure a sustained supply of water for the requisite purposes. Nanotechnology is also being looked upon to provide an economical, convenient and ecofriendly means of wastewater remediation. Different types of nanoparticles such as nanosized metals, metal oxides, zerovalent ions, Nano filtration membranes have proven effective in detection, removal and/or destruction of contaminants.

Nanotechnology used for detection of pesticides, chemical and biological substances including metals (e.g. Cadmium, copper, lead, mercury, nickel, zinc), Nutrients (e.g. Phosphate, ammonia, nitrate, nitrite), Cyanide Organics, Algae (e.g. Cyanobacterial toxins) Viruses, Bacteria, Parasites, antibiotics and Biological agents are used for terrorism. Nanoparticles when used as adsorbents, nanosized zerovalent ions or nanofiltration membranes cause pollutant removal/separation from water whereas nanoparticles used as catalysts for chemical or photochemical oxidation effect the destruction of contaminants present.

Nanoparticles can be produced from larger structures (top down) by use of ultrafine grinders, lasers and vaporization followed by cooling. For complex particles, nanotechnologists generally prefer to synthesize

nanostructures by a bottom-up approach by arranging molecules to form complex structures with new and useful properties.

II. MATERIALS AND METHODS

This prospective comparative study was carried out on the Dairy Industry wastewater in the Department of civil engineering, at Secab institute of Engineering and Technology, vijayapur, Karnataka from -----

Study Design: Environmental Engineering Study

Study Location: This study was related to wastewater treatment done in Department of civil Engineering, at Secab Institute of Engineering and Technology, Vijayapur, Karnataka, India.

Study Duration:

Procedure Methodology:

Water Sample

The water sample will be collected in 5L-capacity plastic can from the dairy industry. The sampled water samples will be stored at $4.0 \pm 2^{\circ}$ C for a period of 48 hrs, since they were collected and kept remained at $4.0 \pm 2^{\circ}$ C until its physicochemical characterization. Physicochemical test were conducted as per standard procedures listed in table 3.1

Analytical methods for physico-chemical characterization

Sl. No.	Physio-chemical parameters	Method applied for laboratory analysis
1	pH	Digital pH meter
2	Total suspended solids	Gravimetric residue drying 100° C
3	Total Dissolved solids	TDS meter
4	Chemical oxygen demand	Potassium dichromate closed reflux method
5	Biochemical oxygen demand	Winkler's Method
6	Dissolved oxygen	Winkler's Method
7	Turbidity	Digital turbidimeter
8	Alkalinity	Titration
9	Hardness	EDTA method

Chitosan

Chitosan was purchased from Hi media laboratories, product description is given below.

Preparation: from shrimp shells

Synonym: Deacetylated chitin; Poly (D-Glucosamine)

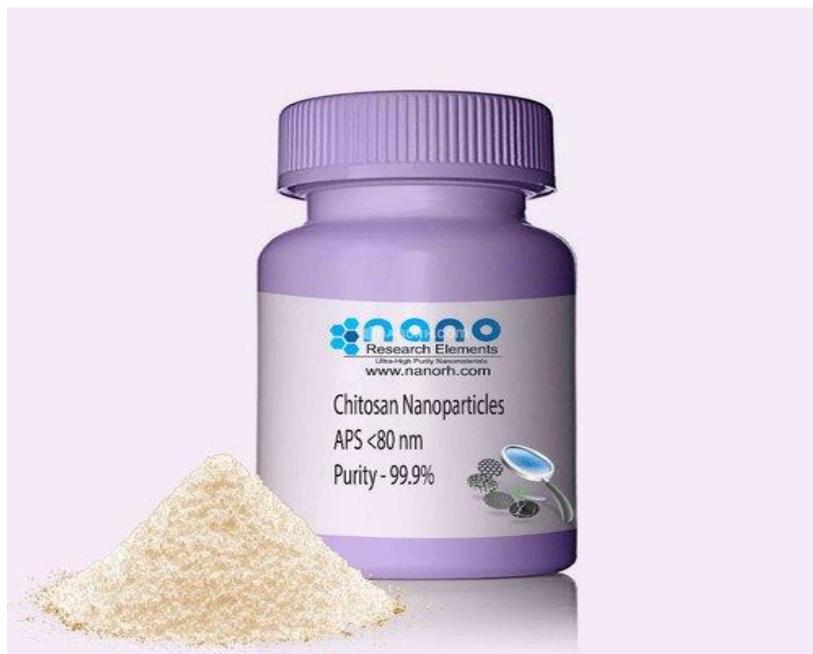
Molecular formula: $(C_6 H_{11} NO_4)_n$

Appearance: Off-white to orange granules or flakes or powder

Solubility: 33.3 mg soluble in 1 mL of dilute glacial acetic acid

Degree of Deacetylation: ≥ 75.0 %

Chitosan powder (100mg) was accurately weighed into a glass beaker, mixed with 10ml of 0.1M HCl solution and dissolved at 60° C temperature with 5 hours continuous stirring. It was then diluted to 100ml with distilled water. This solution should be prepared daily. HCl was considered to be a better choice as acid environment compared to acetic acid to avoid the entrance of organic matter to the sample by acetic acid.



Preparation of Nano-chitosan

Chitosan solution (0.1 M) was prepared by dissolving 16 gm of chitosan in 1L of 2% acetic acid with stirring overnight at 60⁰ C. 36.7 gm of TPP was dissolved in 1 liter of double distilled water to prepare 0.1 M solution. Chitosan nano particles were prepared by adding the chitosan solution drop wise to the TPP solution according to the following ratio (CS: TPP v/v), 1:1. The formed nano chitosan were filtered and washed several times with double distilled water.

Preparation of synthetic turbid water

To prepare turbid water, 10g of kaolin was added to 1L of river water. The suspension was stirred slowly at 20 rpm for 1 h for uniform dispersion of Kaolin particle. The suspension was then permitted to stand for 24 h to allow for complete hydration of the Kaolin. This suspension was used as the stock solution for the preparation of water samples of varying turbidities for the coagulation tests. Low (0-20NTU), Medium (100-200 NTU) and High (>200NTU) turbid water samples are prepared by adding sufficient Kaolin solution to Dairy industry wastewater.

Preparation of Alum solution

Alum solution was prepared by dissolving 10g Alum (Al₂(SO₄)₃.18H₂O) in distilled water and the solution volume was increased to 1 L. Each 1 mL of this stock solution was equal 10 mg/L when added to 1 L of water to be tested.

Experimentation

A conventional jar test apparatus (Figure 3.4) is employed for the tests. A series of jar tests are conducted. All the tests are carried out with 1 L samples. The experiments were run by using synthetic turbid water having low, medium and high turbidities. The pH of water sample was adjusted using hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions. After the coagulant (Alum) was added to the suspension, the beaker was rapidly mixed at 100 ± 2 rpm for 2 min followed by 28 min of slow mixing at 45 ± 2 rpm and afterward the samples were allowed to settle for 30 min. The experiments were done at environment temperature (27°C).

In the first cycle, alum is used as coagulant for comparative study, by varying the pH and dosages, optimum pH and optimum dosages are obtained for low, medium and high turbid waters. In the second cycle, the chitosan was used alone as coagulant and optimum pH and dosages are obtained. In the third cycle, Jar test is run using Chitosan nanoparticles as coagulant. And in the fourth cycle, Chitosan aided coagulant is used for Jar test. The samples were taken from the top 4 cm of the suspension. Percent removal efficiency of nano-chitosan is evaluated by the analysis of number of results obtained.

Jar Test Procedure

The purpose of the laboratory jar test is to select and quantify a treatment program for removal of suspended solids from raw water. Jar tests are conducted six-place gang stirrer, which can be utilized to simulate mixing and settling conditions in a clarifier. Jars (beakers) with different treatment programs or the same product at different dosages are run side-by-side, and the results compared to an untreated jar, or one treated with the current program. The general procedure for jar testing is as follows.

1. Fill 6 number of 1000 mL transparent jars with well-mixed test water, using a 1000 mL graduate.

2. Place the filled jars on the gang stirrer, with the paddles positioned identically in each beaker.
3. Mix the beakers at 40-50rpm. Discontinue mixing until polymer addition is completed.
4. Add increasing dosages of the coagulant to subsequent beakers. Inject coagulant solutions as quickly as possible, below the liquid level and about halfway between the stirrer shaft and beaker wall.
5. Increase the mixing speed to 100-125 rpm for 2 minutes (rapid mix).
6. Reduce the mixing to 40 rpm and continue the slow mix for 28 minutes.
7. Turn the mixer off and allow settling to occur for 30min.
8. After settling for a period of time, note supernatant appearance. If desired, the latter may be quantified using a turbidimeter or clarity wedge (for turbidity), or determined gravimetrically (for suspended solids).
9. Remove the jars from the gang stirrer, empty the contents and thoroughly clean the beakers. 10. Repeat the procedure from Step 1, but vary the pH in increasing order with every beaker but with same optimum dosage of coagulant in all the beakers. Test it for optimum pH.

III. Result And Discussion

Physico-chemical tests were conducted as per standard procedures listed in table 3.1 before Jar testing is started. The initial results are listed in the table 3.1.

Table 3.1: Initial values of the tests for different parameters

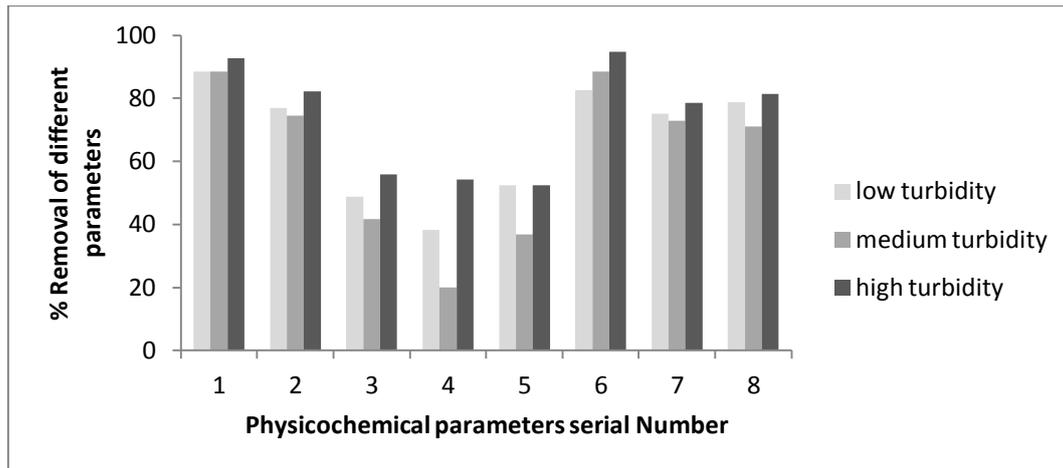
Sl. No.	Physio-chemical parameters	Trial-1	Trial-2	Trial-3	Mean
1	pH	8.1	7.71	7.93	7.91
2	Total Suspended solids	140	137	139.9	138.9
3	Total Dissolved solids	77.9	79	78.1	78.33
4	Chemical oxygen demand	12	11.7	10.3	11.33
5	Biochemical oxygen demand	9.3	8.08	8.88	8.75
6	Dissolved oxygen	8.3	8.1	8.8	8.4
7	Turbidity	17.9	15.6	17.6	17.17
8	Alkalinity	85	93	88	88.7
9	Hardness	143	147	147	145.7

3.1 First cycle of jar tests

In order to determine the optimum coagulant dose & optimum pH required to remove as much turbidity as possible, jar tests were performed in the first cycle with Alum as coagulant. This was run to gain an experience and results for comparison with easily available, most widely used coagulant (Alum) in almost all the water treatment plants. The Jar tests were run between dosages of 10, 20, 30, 40, 50, 60 mg/L. After the Jar test, the supernatant is tested for listed parameters. The results are shown in table 3.2. Percentage removal is depicted in Graph 3.1.

Table 3.2: Results of the first cycle of experiments

Jar test results	Opt. Dosage	Low turbidity	Medium turbidity	High turbidity
	Opt. p ^H	50mg/L	40mg/L	30mg/L
		7.5	7.5	8.5
Total Suspended solids		16	16	10
Total Dissolved solids		18	20	14
Chemical oxygen demand		5.8	6.6	5
Biochemical oxygen demand		5.4	7	4
Dissolved oxygen		4	5.3	4
Turbidity		3	11.5	10.5
Alkalinity (as CaCO ₃)		22	24	19
Hardness (as CaCO ₃)		31	42	27



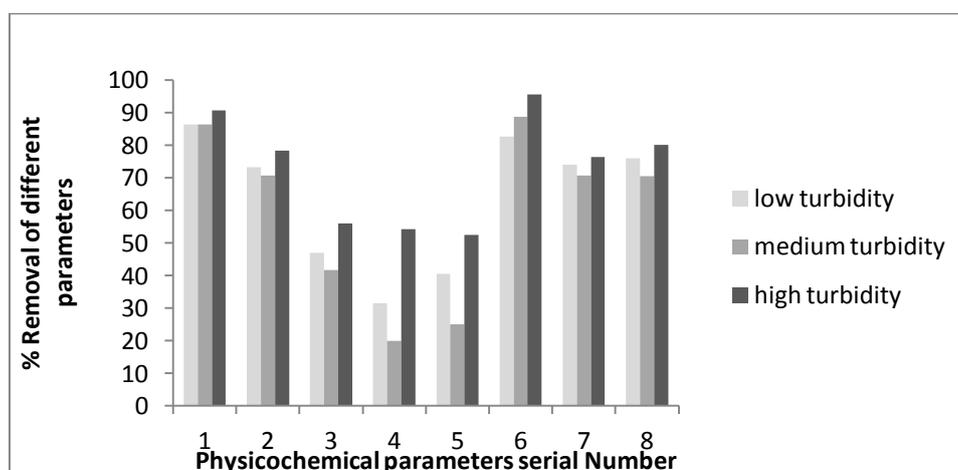
Graph 3.1: Percentage removal in different parameters after Jar test of first cycle

4.2 Second cycle of jar tests

In order to evaluate the efficiency of chitosan biopolymer and to determine the optimum coagulant dose & optimum pH required to remove as much turbidity as possible, jar tests were performed in the second cycle with Chitosan Biopolymer as coagulant. The Jar tests wererun between the dosages of 0.25, 0.5, 0.75, 1.0, 1.25, 1.50 mg/L. After the Jar test, the supernatant is tested for listed parameters. The results are shown in table 4.3. Percentage removal is depicted in Graph 3.2.

Table 3.3: Results of the second cycle of experiments

Jar test results	Low turbidity				Medium turbidity				High turbidity			
	Opt. Dosage		1 mg/L		0.5 mg/L		0.5 mg/L		0.5 mg/L		0.5 mg/L	
	Opt. p ^H		6.5		6.5		6.5		6.5		6.5	
Total Suspended solids			19		19		13					
Total Dissolved solids			21		23		17					
Chemical oxygen demand			6		6.6		5					
Biochemical oxygen demand			6		7		4					
Dissolved oxygen			5		6.3		4					
Turbidity			3		11.3		9					
Alkalinity (as CaCO ₃)			23		26		21					
Hardness (as CaCO ₃)			35		43		29					



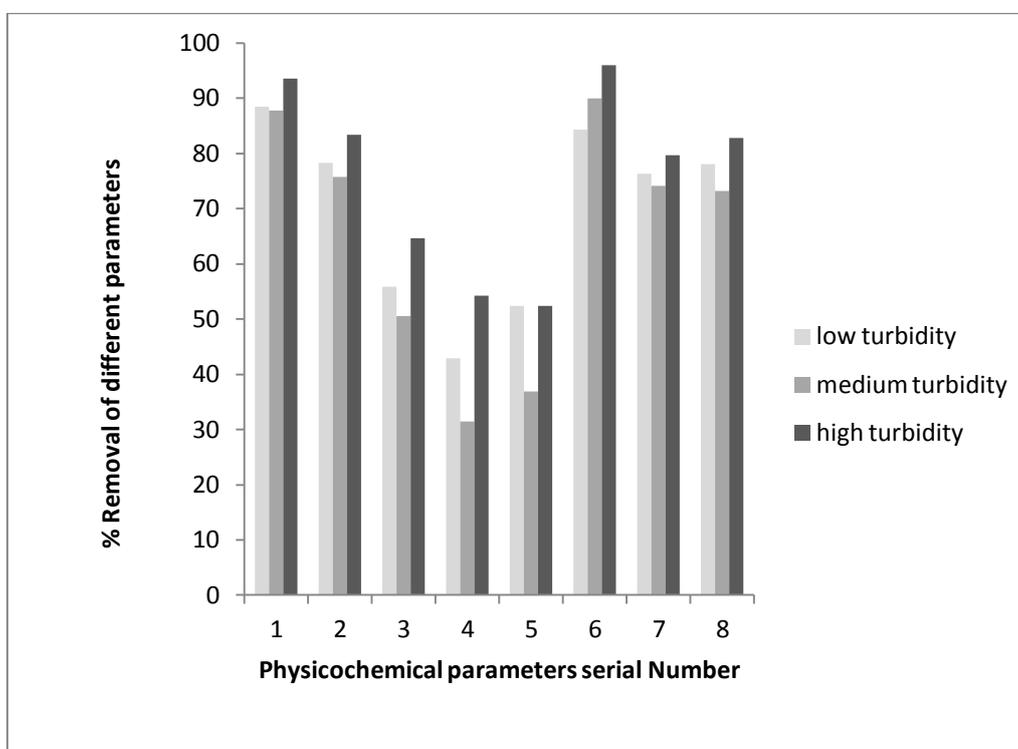
Graph 3.2: Percentage removal in different parameters after Jar test of second cycle

3.3 Third cycle of jar tests

In order to evaluate the efficiency of Nano-chitosan and to determine the optimum coagulant dose & optimum pH required to remove as much turbidity as possible, jar tests were performed in the third cycle with Nano-chitosan as coagulant. The Jar tests were run between the dosages of 0.25, 0.5, 0.75, 1.0, 1.25, 1.50 mg/L. After the Jar test, the supernatant is tested for listed parameters. The results are shown in table 3.4. Percentage removal is depicted in Graph 3.3.

Table 3.4: Results of the Third cycle of experiments

Jar test results	Opt. Dosage	Low turbidity	Medium turbidity	High turbidity
	Opt. p ^H	1 mg/L	1 mg/L	1 mg/L
Total Suspended solids		16	17	9
Total Dissolved solids		17	19	13
Chemical oxygen demand		5	5.6	4
Biochemical oxygen demand		5	6	4
Dissolved oxygen		4	5.3	4
Turbidity		2.7	10	8.1
Alkalinity (as CaCO ₃)		21	23	18
Hardness (as CaCO ₃)		32	39	25



Graph 3.3: Percentage removal in different parameters after Jar tests of third cycle

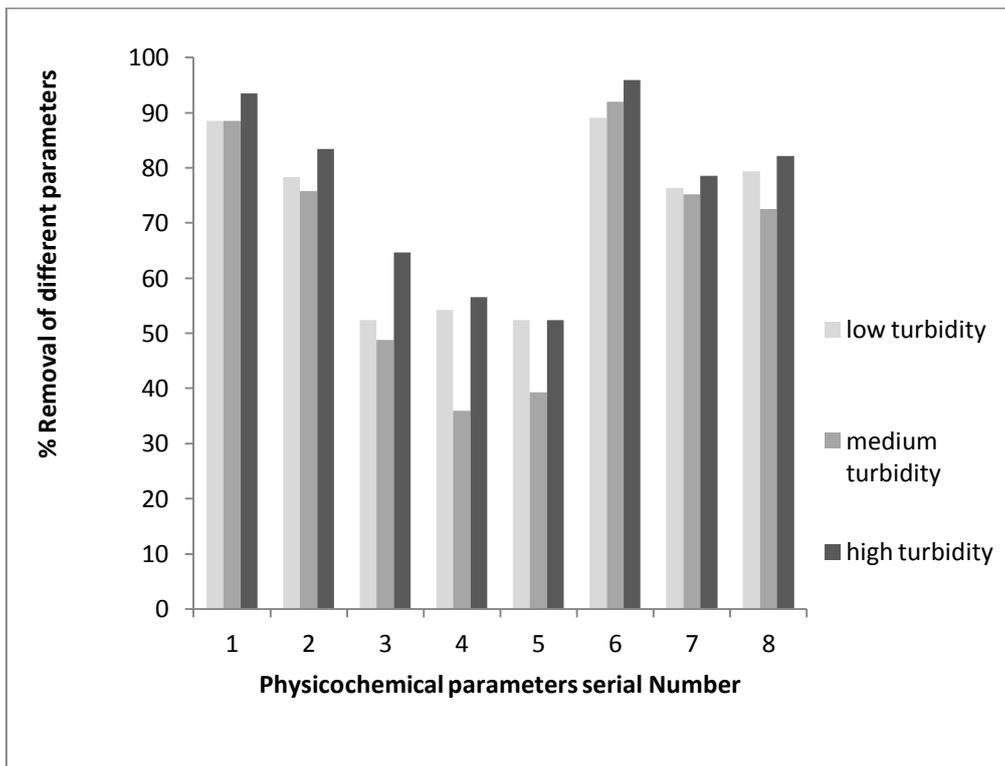
3.4 Fourth cycle of jar tests

In order to evaluate the efficiency of chitosan aided coagulant (Alum + Chitosan) and to determine the optimum coagulant dose & optimum pH required to remove as much turbidity as possible, jar tests were performed in the Fourth cycle with Alum as coagulant and chitosan as coagulant aid. The Jar tests were run between the dosages of alum 10, 20, 30, 40, 50, 60 mg/L with coagulant aid chitosan was added after 1min of stirring with dosages 0.25, 0.5, 0.75, 1.0, 1.25, 1.50 mg/L. After the Jar test, the supernatant is tested for listed parameters. The results are shown in table 3.5. Percentage removal is depicted in Graph 3.4.

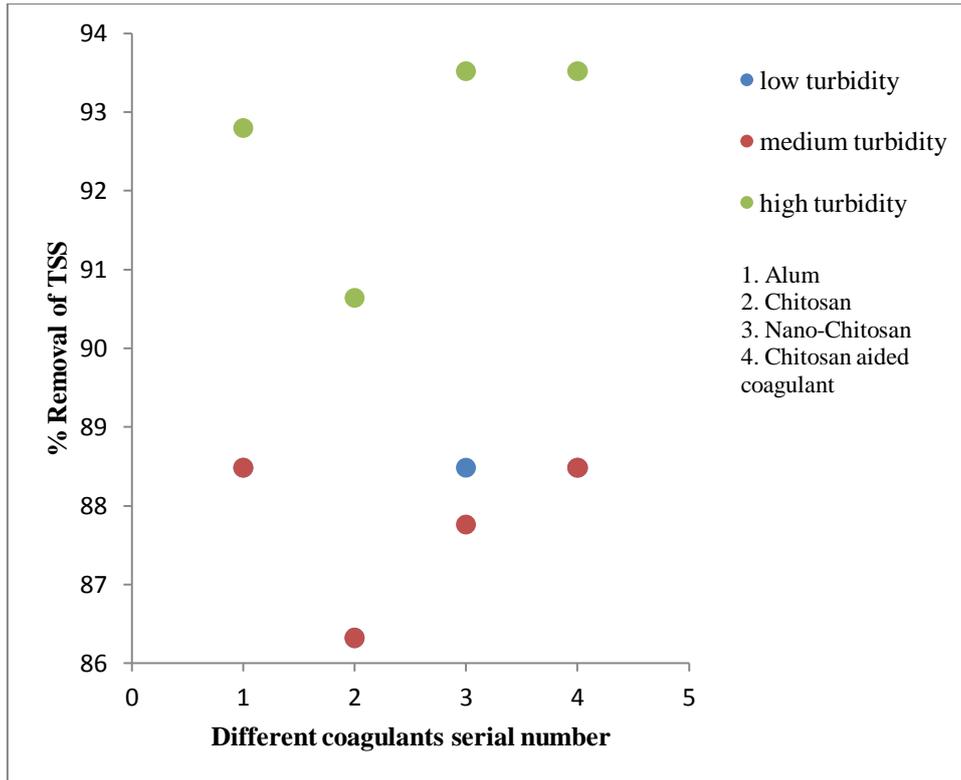
Table 3.5: Results of the fourth cycle of experiments

Jar test results	Opt. Dosage	Low turbidity	Medium turbidity	High turbidity
	Opt. p ^H	30 mg/L	20 mg/L	20 mg/L
Total Suspended solids		16	17	9

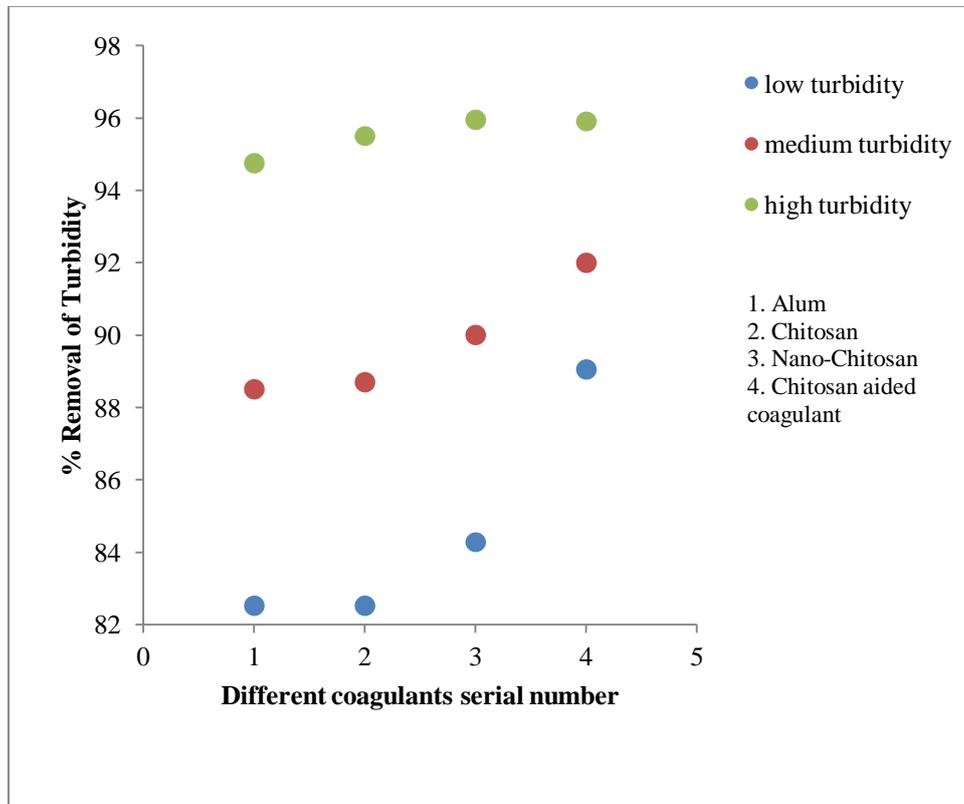
Total Dissolved solids	17	19	13
Chemical oxygen demand	5	5.6	4
Biochemical oxygen demand	5	6	4
Dissolved oxygen	4	5.3	4
Turbidity	1.88	8	8.2
Alkalinity (as CaCO ₃)	21	23	18
Hardness (as CaCO ₃)	32	39	25



Graph 3.4: Percentage removal in different parameters after Jar tests of fourth cycle



Graph 3.5: Comparison of removal of TSS from different coagulants



Graph 3.6: Comparison of removal of turbidity from different coagulants

IV. Conclusion

1. It can be observed from results that Nano chitosan has shown better removal efficiency in almost all the parameters. For highly turbid water, alum & chitosan showed the removal efficiency of turbidity of 94.75% and 95.5% whereas Nano-chitosan removed turbidity at 95.95%. And when it was tested as a coagulant aid, chitosan behaved very efficient in removal of turbidity (95.9%) and also this decreased the dosage of alum efficiently.
2. For highly turbid water, alum & chitosan showed the removal efficiency of TSS of 92.8% and 90.64% whereas Nano-chitosan removed TSS at 93.52%. And when it was tested as a coagulant aid, the removal efficiency of TSS was shown 93.52% and also it decreased the dosage of alum efficiently.
3. Chitosan can be used as coagulant aid with alum.
4. Nano-chitosan showed the better removal efficiency than alum & chitosan biopolymer in almost all the parameters and in all types of turbid waters.
5. Nano-chitosan can be suggested for treating turbid waters as also prevents the accumulation of aluminium salts in the environment.

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