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RESEARCH ARTICLE

CHITOSAN: AN EFFECTIVE MATERIAL FOR TEXTILE WASTE WATER MANAGEMENT

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Abstract

In recent years dye removal by environmentally friendly, low-cost adsorbents from textile wastewater are in demand. Many researchers have focused on low cost bio-materials like cellulose, alginate, chitosan and lignin. But till today no such materials have found commercial significance in wastewater treatment. Very less work is found which is carried on real life waste water. As being the second largest biodegradable polysaccharide, chitosan has gained preferred interest than others in diversified fields including textile. Chitosan possesses a cationic character in acidic medium enabling its dissolution and possibilities of ion- exchange interactions with anionic compounds. This offers the probability of acting as a sequestrant and can also undergo chemical modifications yielding a large variety of useful derivatives. In this research work, chitosan was dissolved using acetic acid at different concentrations to observe the effect of chitosan dosage in textile effluent parameters obtained from a local factory. Results revealed that chitosan could successfully be used to coagulate and flocculate anionic suspended solids to lower down the TDS, COD, BOD values and more effectively used as a bio-adsorbent to remove color from the wastewater. The highest chitosan performance was obtained with 60ml of 0.05% and 0.1% chitosan solution which reduced the polluted water characteristics like COD, BOD, and TDS below the maximum discharge value with a significant reduction in color

Introduction:-

Effluent is "an out flowing of water or gas to a natural body of water, from a structure such as a wastewater treatment plant, sewer pipe, or industrial outfall"(Wikipedia, 2019, November)

Significant volumes of effluent are being generated by the consumption of large quantities of process water needed in different steps of dyeing and finishing processes. Water from the dyeing and printing units are highly colored containing residual chemicals like acids and alkalis, salts, various organic and inorganic chemicals. These contaminants are ecologically toxic and when discharged untreated into the surrounding can give rise to severe effects in the long run (Z. Wang, Xue, Huang, & Liu, 2011). Their toxic effect is well recognized by the society and

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thus increased interest in ecologically friendly processes is escalating. One of the main challenges faced by the textile sector today is to modify the existing production processes to a more environmentally friendly process, which will be competitive in price and at the same time use greener or safer dyes and chemicals – thereby reducing the cost of effluent disposal. It is essential to implement stringent control measures to reduce effluent problems. Recycling is not an option anymore but rather a necessity to control pollution (Babu, Parande, Raghu, & Kumar, 2007).

Segregation of the wastewater is done based on the nature of the different chemicals employed for the different industrial processes. Chemical contaminants are introduced from the raw materials and also from the different additives applied to produce the final finished product. Contaminants of environmental concern range from intense colored synthetic organic dyes which are non-biodegradable to insecticide from insect proof finishing (Aouni et al., 2012). High concentrations of organic and inorganic chemicals are characterized by high Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Total Dissolved Solids (TDS), pH, Total Suspended Solids (TSS) values and low Dissolved Oxygen (DO) (Morshed, Al Azad, Alam, Shaun, & Deb, 2016). Even though the dyes are present in small quantities in effluent but nevertheless it severely affects the aesthetic characteristic of water and also makes it opaque which in turn disrupts the marine environment when discharged in rivers and lakes (Chequer et al., 2013). In addition degradation products of some dyes are carcinogenic and toxic, thus their removal cannot rely on bio-degradation alone but needs a well-planned decolorization process through the removal of dyes in the wastewater treatment (O. J. Hao, Kim, & Chiang, 2000; Kannan & Sundaram, 2001).

BOD values and total suspended solids can be effectively reduced by the standard industrial effluent treatment process of applying activated sludge and sedimentation. But the process fails to remove the color efficiently. Thus there is an exigency to develop technology that is both cheap and biocompatible (Trung, Ng, & Stevens, 2003). Various methods including chemical precipitation (X. Hu et al., 2010), nano-filtration (Al-Rashdi, Johnson, & Hilal, 2013), solvent extraction (Černá, 1995), ion exchange (Vaaramaa & Lehto, 2003), reverse osmosis (Zhang, Zhao, Wei, & Li, 2014), and adsorption (Coşkun, Soykan, & Saçak, 2006) have been extensively studied in the recent decade to remove pollutants from the contaminated waters. Out of all these methods, adsorption is particularly attracting scientific focus mainly because of its low cost, high efficiency, easy handling and abundance of different adsorbents (M. Ahmad, Ahmed, Swami, & Ikram, 2015).

Some of the biomaterials which are in scientific focus for the treatment of wastewater include cellulose (Phan et al., 2006), alginate (Ahmed & Ikram, 2015), chitosan (Ahmed, Ahmad, & Ikram, 2014) and lignin (Ehara, Saka, & Kawamoto, 2002). These materials are not only cheap, non-toxic, biodegradable but are also available in abundance (M. Ahmad et al., 2015). Chitosan in particular has gained much attention due to its potentiality to replace hazardous chemicals used in wastewater treatment. Earlier investigations have shown that they could be used as coagulating/flocculating agents for polluted wastewaters (Ali, Laghari, Ansari, & Khuhawar, 2013), in heavy metal or metalloid adsorption (Cu(II), Cd(II), Pb(II), Fe(III), Zn(II), Cr(III), etc.) (Tran, Dai Tran, & Nguyen, 2010; Wan, Kan, Rogel, & Dalida, 2010; L. Wang et al., 2010), for the removal of dyes from industrial wastewater (i.e. textile wastewaters) (El Mouzdahir, Elmchaouri, Mahboub, Gil, & Korili, 2010; Hadi, 2013), as well as for the removal of other organic (i.e. pollutants such as organochloride pesticides, organic oxidized or fatty and oily impurities. Due to the high performances, chitosan derivatives are used as adsorption additives (Zuo, 2014).

Chitosan is a linear polysaccharide composed of randomly distributed β-(1→4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). It is a non-toxic, biodegradable polymer of high molecular weight and is very much similar to cellulose. It is a versatile chemical because of the presence of some intrinsic properties like biodegradability, polyfunctionality, biocompatibility, hydrophilicity, film-forming ability and adsorptivity (Rinaudo, 2006). Chitosan possesses positive ionic charges in acidic solution, which gives it the ability to chemically adhere with negatively charged dyes, fats, lipids, cholesterol, metal ions, proteins, and macromolecules (Q. Li, Dunn, Grandmaison, & Goosen, 1992; Wikipedia, 2020, April 15). But the application of chitosan to cohere anionic colorants is somewhat confined at neutral and alkaline medium due to the minimal protonation of the amino groups of chitosan along with the low approachability of protonated amino groups within the crystalline structure (Cho, No, & Meyers, 1998; Trung et al., 2003). In most solvents chitosan does not have any solubility but dissolves in dilute organic acids like formic acid, succinic acid, acetic acid or malic acid at lower pH than 6.0. Chitosan can be considered as a strong base due to the presence of a number of primary amino groups with a pka value of 6.3. Since the amino groups can be cationized in the presence of acids, it specifies that pH can significantly influence the charged state and properties of chitosan (Grenha, Al-Qadi, Seijo, & Remuñán-López, 2010). At lower pH the amino groups can get protonated and attain a positive charge which in turn converts the chitosan into a water-soluble cationic polyelectrolyte. Conversely, as the pH is raised above 6 these cationic amine groups will start to lose this charge and get deprotonated which will lead to insolubility (Ahmed et al., 2014). The alteration between solubility and insolubility occurs at the pKa value between pH 6 and 6.5. Thus the solubility of chitosan is highly dependent on the degree of deacetylation of the acetyl group and their distribution along the polymer chain, molecular weight of chitosan and the deacetylation method (Rinaudo, 2006; Yi et al., 2005).

Colloidal suspensions are distinguished by the existence of small charged particles of similar nature well dispersed in the solution. Since the dispersion possesses the same charge, the particles repel each other and do not aggregate, producing a stable suspension. The principle of coagulation is to destabilize this suspension by neutralizing the charges causing the particle to aggregate. Chemical coagulants like aluminium sulphate (alum), poly (aluminium chloride) or ferric sulphate are commonly used to enhance coagulation into larger particles called microflocs. These readily available chemicals which are prone to produce environmental hazards and create a need for an eco-compatible substitute based on biodegradable and renewable materials like chitosan, alginate or tannins.

The next step requires flocculation of the agglomerates. Flocculation involves the conversion of small, destabilized particles into larger flocs with the use of high molecular weight polymers, called flocculants, which can clump them and makes it easier for their separation from water. Flocculants form a network entrapping the particles, facilitating agglomeration, acting as a net that makes sedimentation easier. Subsequently, chitosan can function as a linking species to act as a nucleus forming macroflocs, which eventually agglomerates and settle down (Butola, 2018; J. Li, Jiao, Zhong, Pan, & Ma, 2013; J. Li, Song, et al., 2013). Coagulation in conjunction with flocculation assists in water clarification. As chitosan is a high molecular weight compound it can efficiently execute the role of both coagulant and flocculant (Butola, 2018; "Coagulation and Flocculation Process Fundamentals "; "Flocculation," 2020, April 11).

In this study, the viability of using chitosan as a bio-absorbent for the reduction of pollutants directly from a textile wastewater plant was assessed. Emphasis has been given to the removal of colorants, COD, BOD and TDS from effluent, produced from a combined physico-chemical treatment plant in a local cotton industry.

Experimental:

Sample collection:

Real life wastewater samples were collected from the discharge point after being aerobically treated from a local factory, Liberty Knitwear Ltd (Un-2), situated in Chandra, Gazipur, Dhaka. The collected samples were kept at ambient temperature before assessment.

Chitosan solution preparation:

500mg of chitosan powder was dissolved in 100 ml of glacial acetic acid (10%) solution to yield a 0.5% stock solution by stirring with a magnetic stirrer with an approximate rpm of 100 until all the powder was dissolved completely. Since chitosan takes time to dissolve the solution was mildly heated to accelerate the dissolution. Testing reagents were then produced by dilution of this stock with distilled water to the desired concentration. 0.05%, 0.1%, 0.15% and 0.2% chitosan solutions were prepared. From each of this 40ml, 60ml and 80ml solutions were respectively used in the treatment of 100 ml wastewater obtained from the factory.

The flocculation process with respect to varying amount of chitosan dosage (40 ml, 60 ml, and 80 ml) was observed, keeping the rest of the parameters constant such as pH (5-5.5) and mixing time about 60 minutes.

Analytical Methods:

PH of the wastewater was measured using Hanna portable digital pH meter made in china, which was first calibrated using a buffer solution of pH 4.0 and 7.0 before measuring the samples. Similarly TDS was also measured using TDS meter by Fernox UK. COD analysis was carried out in a cell test from MERCK (denominated kits) USA. These tubes contain the required reagents for the oxidation (potassium dichromate, sulphuric acid and silver sulfate). While BOD was estimated using the standard procedure of measuring BOD_5 where dissolved oxygen concentration is measured over an incubation period of 5 days at 20^0C. UV–vis absorption using an HP 8453 spectrophotometer from Germany was used to determine SAC (spectral absorption coefficient) values (1 cm cell width) after filtration of samples with a 0.45 μm filter, according to the ISO 7887:1994 method.

Results and Discussion:-

Studies on the effects of chitosan dosage in varying concentrations but at constant pH and mixing time were carried out to investigate the coagulation and flocculation capacity of chitosan in waste water treatment process. The table below represents the characteristic of the discharge water collected from the outlet of the factory and the permissible DOE Standards for discharge into an inland surface water body by the Ministry of Environment and Forest, Bangladesh ("Guide for Assessment of Effluent Treatment Plants," June 2008).

Table I:- Characteristic of discharge water and permitted quantity.

Parameters	Discharge quantity	Permitted quantity
TDS mg/l	2194	2100
COD mg/l	385	200
BOD mg/l	140	50
Color (Pt/Co)	2565	-

Chitosan dosage:

The most important parameter considered here was the dosage of chitosan to determine the best suitable circumstances to bring about the maximum performance of chitosan to coagulate and flocculate. Neither insufficient dosing nor overdosing would give the actual performance of chitosan to flocculate. Therefore, it is critical to find out the optimum dosage to get the best performance out of chitosan along with a reduction of dosing cost. The effect of dosing was analyzed after reducing the pH of the wastewater to pH 5-5.5 and adding 40 ml, 60 ml, 80 ml of 0.05%, 0.1%, 0.15% and 0.2% chitosan solutions to 100ml water.

Effect of chitosan concentration on TDS level:

Total dissolved solids (TDS) measures the combined dissolved content of all organic and inorganic materials present in molecular, colloidal, ionized or suspended form ("Total Dissolved Solids,"). Total dissolved solids (TDS) enclose the unfilterable materials in water; they are so-called because these particles can easily pass through existing filters (2-micrometer or less) during filtration because of its minute size (Crotts, 1996). The results of chitosan dosage on TDS are presented in figure 1.

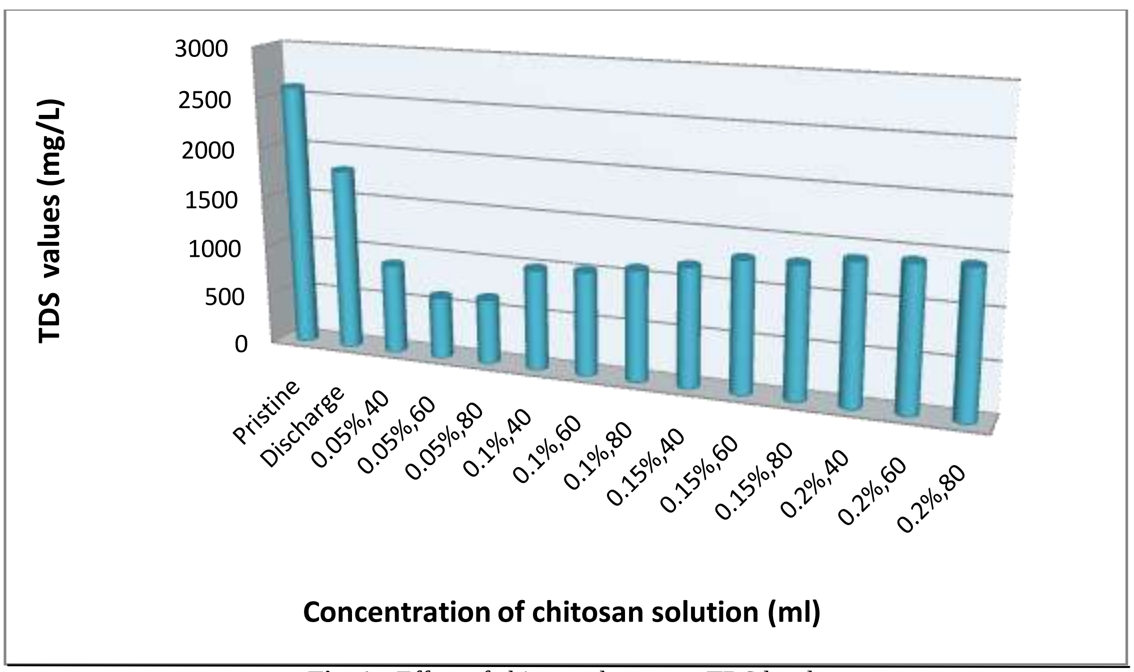

Fig. 1:- Effect of chitosan dosage on TDS level.

It is evident from the results that a significant decrease is noticed for 0.05% concentration of chitosan for any amount. The highest reduction of TDS was obtained when treated with 60 ml of 0.05% chitosan solution. But with further increase in concentration decreases the TDS removal. This can be explained through the charge density distribution of chitosan. Normally chitosan has a high charge density (Kumar, 2000). When chitosan dosage is increased above 0.05%, the TDS removal gradually decreases because the adsorbent may have filled the colloidal surfaces leaving very little or no room for further bridging (Abdullah & Jaeel, 2019).

Effect of chitosan concentration on COD level:
For 0.05% dosage, the percentage of reduction for COD was increased as presented in Figure 2. The highest reduction of COD was obtained when treated with 60 ml of 0.05% chitosan solution. This phenomenon can again be attributed to the charge density of chitosan (A. Ahmad, Sumathi, & Hameed, 2006). The charge density increases as adsorption increases leading to rapid destabilization of particles (Ariffin, Shatat, Norulaini, & Omar, 2005). Thus lower amount of chitosan is suitable as a coagulant to destabilize particles due to high charge density.

Further increase in chitosan concentration/amount leads to a fall in the reduction of COD. This may be due to the fact that excess polymers are adsorbed on the colloidal surfaces and again produces stabilized colloids. These re-stable colloids attain positive charge thus repelling each other in suspension.

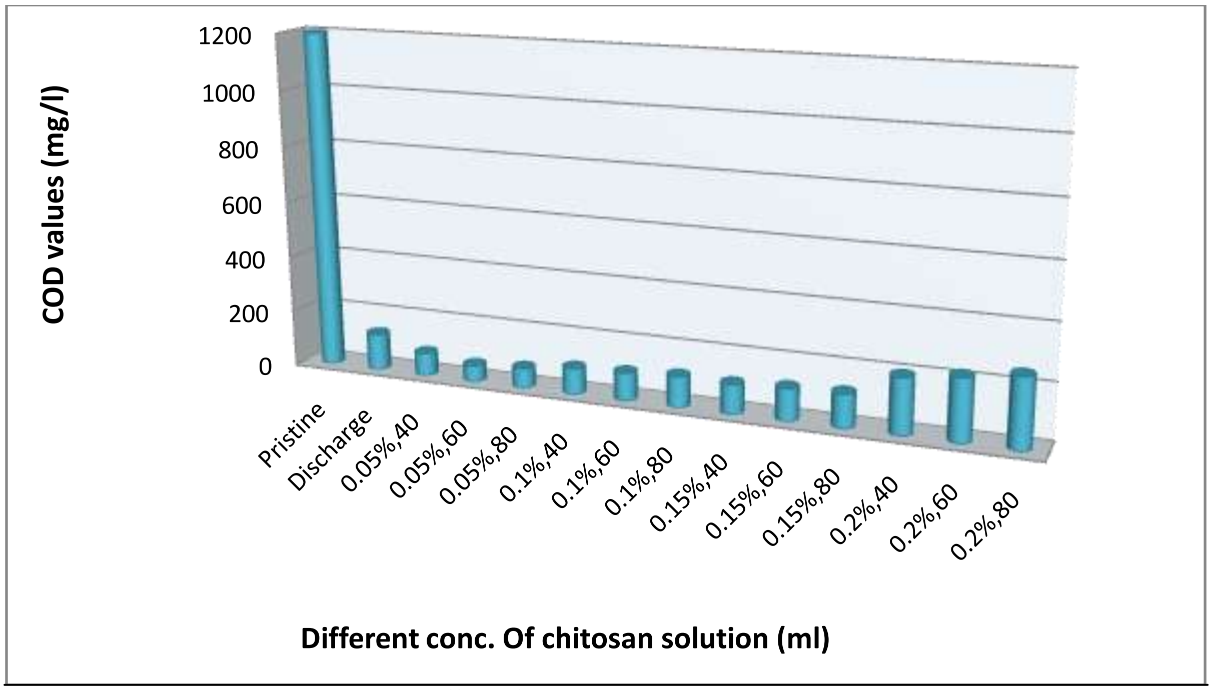

Fig. 2:- Effect of chitosan dosage on COD values.

Effect of chitosan concentration on BOD level:
No major change was noticed in the BOD value as compared to the discharged amount. But even in this case the ideal dosing is seen for 0.05% concentration. Like COD higher charge density with increased concentration of chitosan may have limited the reduction of BOD.

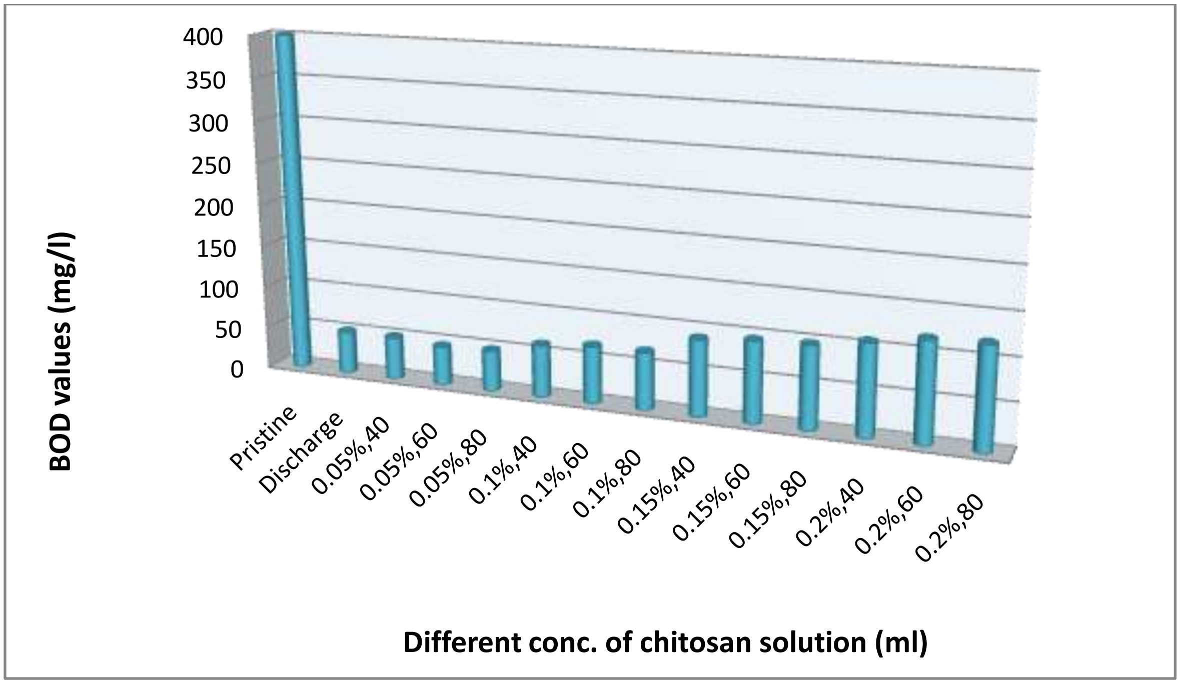

Fig. 3:- Effect of chitosan dosage on BOD values.

Effect of chitosan concentration on color removal:

Figure 4 shows the impact of chitosan dosage on the removal of color. The discharge water from the factory was not treated with any decolorant. It is evident that large amounts of color can be removed with the bio-adsorbent chitosan as seen from the graph. Around 85% color was reduced from the discharge wastewater by optimum dosing of 60ml of 0.1% chitosan solution. The sorption ability of chitosan is said to be at its maximum at pH 4-5 when it can electrostatically interact with the anions of the solution (Guzman, Saucedo, Revilla, Navarro, & Guibal, 2003). As stated by many researchers (Y. Hao, Yang, Zhang, Hong, & Ma, 2006) that 90% of the surface NH_2 functional groups get protonated at pH 4 which gradually decreases to around 50% with the increase of pH to 6. Therefore, an appreciable decrease in the positive charge will occur with the increase in pH, thus the ability of chitosan to destabilize the particles by neutralization is compromised. It is this cationic nature of chitosan that is utilized for both coagulation of anionic compounds and the flocculation of particles.

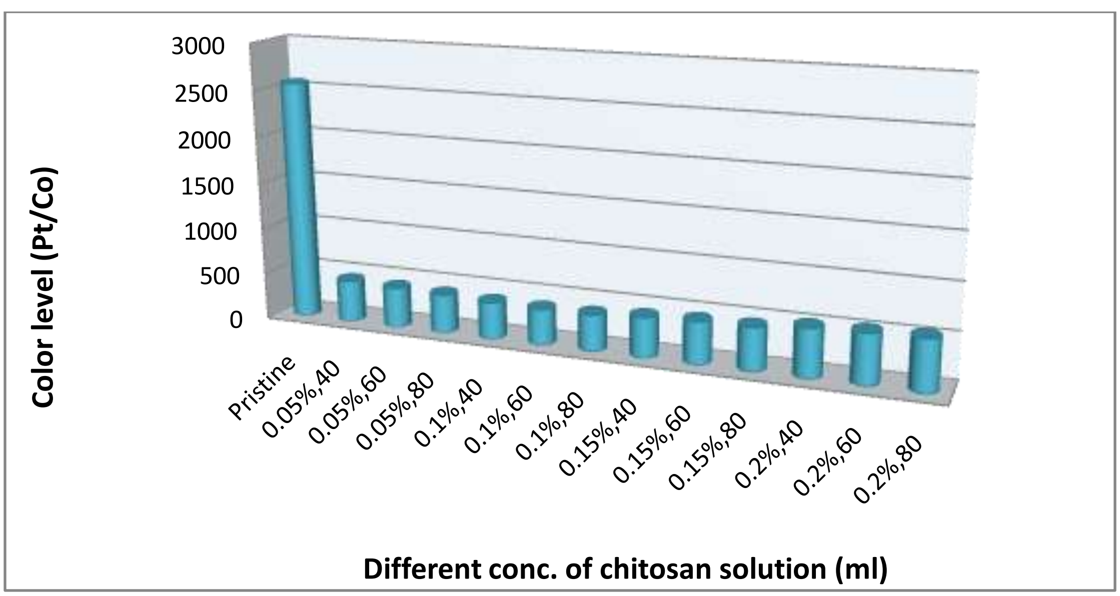

Fig. 4:- Effect of chitosan dosage on color level.

Conclusion:-

Chitosan is an economically feasible material since it can be produced easily with cheap chemical reagents. From the proven properties it can be stated that this polymer can be an effective alternative to the conventional, costly and environmentally toxic adsorbents that are presently in use, posing as a highly promising additive for wastewater pollutants. Another advantage of this bio-polymer based adsorbent is that they do not produce any hazardous by-products during thermal degradation as the traditional synthetic resins. The scope of modification of this polymer chemically or physically to improve its applicability in different medium gives it the potential to be an excellent candidate for wastewater treatment.

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