

BIODEPOLLUTION OF PAINT MANUFACTURING INDUSTRY WASTE WATER CONTAINING CHROMIUM BY USING COAGULATION PROCESS

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ABSTRACT

Heavy metal, chromium (VI) removal by coagulation using natural coagulant material was investigated in this paper. Chromium occurs naturally in the paint manufacturing industry waste water in many steps of the process. The coagulation and flocculation method is used for chromium removal from waste water using fruits of *Opuntia Ficus indica*, Fruits of *Jatropha gossypifolia* and peel of *Borassus flabellifer*. The effects of coagulant type, pH, initial concentration and dosage on removal efficiency of Chromium are determined by spectrophotometrically after sedimentation and filtration in the effluent. Fruits of *Opuntia Ficus indica*, effectively removing chromium from effluent and it was determined as the most effective and economic coagulant type because it requires lower amounts than the other coagulants used in this experiment. The study established that water pH has the greatest impact on the removal of iron-organic complexes from water. Iron-organic complexes (including chromium) are best eliminated from water when its pH is from 6.0 to 7.0.

Keywords: Natural coagulants, chromium (VI), Fruits of *Opuntia Ficus indica*, Fruits of *Jatropha gossypifolia*, peel of *Borassus flabellifer*

INTRODUCTION:

Paint manufacturing industries in India has made tremendous strides in developing newer and quicker processing techniques. The industry has switched over to usage of chromium in manufacturing and processing units. The effluent contains hexavalent Chromium and trivalent Chromium. There are various methods are available for removal chromium from waste water such as reduction, precipitation, ion- exchange, evaporation, reverse osmosis and direct precipitation. Most of these methods need high capital cost which are not suitable for small scale industries.

The present study is undertaken with a view to assess the suitability of using biologically based coagulants for removal of chromium (VI). The studies are carried out with respect to coagulant dosage, pH, initial concentration of chromium, and other physical characteristics properties of water.

LITERATURE REVIEW:

Ravikumar et al., 2013, in his research paper, presented the usage of *moringa oleifera* seeds as coagulants for the removal of cadmium, chromium, copper and lead. They discussed about poly electrolytes nature of coagulants, adsorption charge, neutralization and interparticle bridging of *moringa oleifera* seeds.

Mohd omar Fatehah et al., 2013, studied about total solids removal by applying various naturally available starches as coagulants. Along with natural coagulants two commercial coagulants are applied for removal of TDS from semi conductors' industry waste water. They found the removal efficiency by natural coagulants was almost similar to commercial coagulants.

Vikashni Nand et al., 2012, presented a research paper on using locally available *moringa oleifera*, *Arachis Hypogea*, *Vigna Unguiculata*, *Vigna Mango* and *Zeamays*, for removal of copper, lead, cadmium and zinc. They found that *moringa oleifera* is effective compared to other coagulants.

Abdelaal et al., 2004, studied about treatment of mining waste water by using Bentonite material. In this study water clarity, COD and percent of Suspended Solid removal was carried out. The study indicated that Bentonite is an effective and economical coagulant for removing toxic matters inside the crystals of Benotonite.

Sago a product from milk of tapioca root or *manihot esculenta*, *Cratz. M. utilisssma* and *Hyacinth* bean and *Dolichos Lablab* are used as coagulants for removal of turbidity and to improve the quality of water for drinking purpose. Saritha vara, 2012, found that with 1 mg/L beans removed 87% turbidity at pH 6, followed by 1 mg of sage is 82% at same pH.

Saidu et al., 2013, used *moringa oleifera* for treating waste water, containing heavy metals such as Cadmium and Lead. Metal ions removal was observed ranging from 70.86-89.4%, for lead 66.33 -92.14%, for iron 44.95-47.73% for cadmium.

Chito Ko.Ko. et al., 2012, used *moringa oleifera* seeds for removal of Arsenic from ground water. In this study along with *moringa oleifera* seeds they have taken Alum as commercial coagulant and percentage removal of Arsenic by *moringa oleifera* seeds were compared with Alum.

Parkinosia acculeata and *Vigna unguiculata* are used for removal of suspended particles and fluoride removal from surface water by Annika Blix, 2011. They showed similar efficiency as with that of Alum. Natural coagulants produce less sludge compare to chemical coagulant alum. In this study they removed only suspended solids but not fluoride and turbidity.

Kihampa et al., 2011, reports the performance of *Solanum incunum* L, as natural coagulant and disinfectant for water purification. By these experiments they concluded that *Solanum incunum* L, has efficiency to remove turbidity. The percentage removal of turbidity is in between 75-97%.

Many of the previous investigation stressed on using only *moringa oleifera* as natural coagulant as it is easier, traditional and widely accepted technique. But there many herbal and natural coagulants which can be efficiently used for modifying the physic-chemical characteristics of waste water and improving the quality of water. So the present research work aims to investigate the medicinal, herbal and natural coagulants for removal of heavy metals.

MATERIALS & METHODS:

All the reactive and chemical substances used in this investigation were analytical grade and double distilled water was used in all the experiments to prepare working solutions. As a precautionary exercise standard procedures were followed for sample handling and collection (APHA 1998). All cleaned glassware were soaked in 10% HNO₃ overnight for metal analysis and washed with distilled and deionized water before they were used. The analysis of the samples were carried out soon after collection and stored in a refrigerator for further

analysis. The calibration standards of metals were prepared according to the Standard Methods for Examination Water and Wastewater analysis (APHA 1998).

SELECTION OF COAGULANTS:

Fruits of *Opuntia Ficus indica*, Fruits of *Jatropha gossypifolia* and *Borassus flabellifer* are selected as coagulants for the present study. *Opuntia Ficus indica* is a species of cactus and it is used as a folk medicine for the treatment of burns, wounds, edema and indigestion. Its alcoholic extract possesses anti inflammatory hypoglycemic and anti viral activities. It contains D. Glucose, D-Galactose, L-Arabinose, D-Xylose, L-rhamanose and D-galactaric and glucuronic acids. It contains proteins, flavonoids, penduletin iutocolin, kacepternol, quercetia and quercetin and retin. In the present study opuntia ficus indica is selected as natural coagulant for the removal of Chromium from paint manufacturing industry waste water due its polyelectrolytic nature. It is also used as adsorbent for the removal of color from the textile industry waste water. Another natural coagulant used for removal of chromium from paint manufacturing industry waste water is fruits of *Jatropha gossypifolia*. It belongs to Euphorbiaceae family. Chemical composition of fruit is 2,3 bis-(hydromethyl)-6-7-methylenedioxy-1(3,4, dimethoxyphenyl)-nophthalene, cyclogossino A and B, gossypidin, gossypifan, hydroxyl jatrophone, jatrophol A and B. The latex from the stem of *Jatropha gossypifolia* is known to have coagulant activity and its mechanism of action as haemostatic agent found to be by precipitation of coagulant factors (Oduola et al., 2005). In Nigeria the latex of *Jatropha gossypifolia* is routinely used by herbalists and some peoples in urban centres use it to stop bleeding from nose, gums and skin. *Jatropha gossypifolia* has no adverse effect on the functions of liver kidney and bone marrow. The findings have been carried on mammals and findings of this study can be extrapolated to human as a haemostatic agent (Mane et al., 2011; Song et al., 2004). Taking all these factors into consideration the fruit of *Jatropha gossypifolia* taken as natural coagulant for the removal of chromium from paint manufacturing industry waste water. Another natural coagulant used in the study is fruit peel of *Borassus flabellifer*

PREPARATION OF COAGULANT:

Fruits of *Borassus flabellifer* were purchased in local market of Hyderabad, Andhra Pradesh. Peel of the fruits were removed and cleaned with tap water. After that it was cleaned two times with double distilled water and dried under sunlight for 72 hours. After drying it was ground into fine powder and stored into plastic bags until use. The second natural coagulant in present study is fruits of *Jatropha gossypifolia*. These were collected from the plants of *Jatropha gossypifolia* from the place of Gurranguda forest nearby Hyderabad, Ranga Reddy District and used as natural coagulant for the removal of Chromium from paint manufacturing industry waste water. Another coagulant used for removal chromium in present studies is Fruits of *Opuntia Ficus indica*. These were collected from the plants *Opuntia Ficus indica* from the place of Teldevarapalli Nalgonda district Andhra Pradesh and used as natural coagulant.

PREPARATION OF CR (VI) SOLUTION:

A stock solution of Cr (VI) (3.5 gm ml^{-1}) was prepared by dissolving appropriate quantity of AR grade $\text{K}_2\text{Cr}_2\text{O}_7$ in 100 ml of distilled water from Millipore purification unit. The stock solution was further diluted with distilled water to desired concentration for obtaining the test solutions. Final residual metal (Cr (VI)) concentration after coagulation was directly measured by using Lambda Scientific UV- Visible spectrophotometer.

The experiments are carried out with respect to coagulant dosage, effect of pH on coagulation, effect of initial concentration of chromium on coagulation and other physical characteristics such as pH, Electro conductivity, Salinity, Turbidity, Alkalinity, Acidity, Total Dissolved Solids and Total Hardness of the waste water.

RESULTS & DISCUSSION:

DETERMINATION OF OPTIMUM COAGULANT DOSAGE:

A comparative study has been shown in figure-1. For all these studies, the initial concentration of chromium is 20 mg L^{-1} was maintained and the amount of coagulant was varied between 0.4 gm L^{-1} - 2.2 gm L^{-1} . The results indicate that all these coagulants have capacity to remove Cr (VI). The optimum dosage is 01 gm L^{-1} for *Jatropha gossypifolia* and it is 1.5 gm L^{-1} for *opuntia Ficus indica* and *Borassus flabellifer* peel. Mechanism and principle behind this experiment is the positive charge on Chromium serves as a bridge among anion poly electrolyte. *Opuntia Ficus indica* is the source of viscous natural polyelectrolyte bearing negative surface

charge. The polyelectrolyte nature of *Opuntia Ficus indica* will cause dissociation and develop a charge which will attract the Cr (VI) ion. (Olivera et al., 2001), revealed that the flocculation process induced by anionic polyelectrolyte such as the natural polyelectrolyte extracted from *Opuntia Ficus indica*. The positive metals ion serves to form a bridge among the anionic polyelectrolyte and negatively charged functional groups on the colloidal particle surface. Cactus mucilage is a neutral mixture of approximately 55 high-molecular weight sugar residues composed basically of arabinose, galactose, rhamnose, xylose, and galacturonic acid. This natural product was characterized for its use as a flocculating agent (Ayers et al., 1985). This technique is innovative and it uses natural eco friendly agent in the treatment of drinking water.

Trace amount of latex present in fruit of *Jatropha gossypifolia* act as precipitating agent and destabilizes the protein solution because of continuous shaking. Then the protein which is destabilized colloids with Chromium Cr (VI) and submicroparticles generate and these particles grow under Brownian diffusion process. This process continuously takes place flocculation occurs.

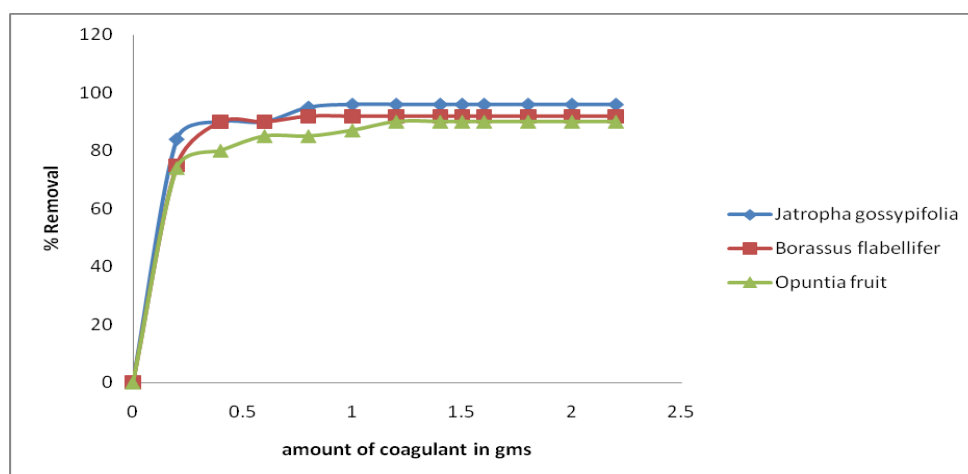


Figure- 1: Effect of Coagulant dosage on removal of Chromium

EFFECT OF INITIAL CHROMIUM CONCENTRATION ON COAGULANT:

The percentage removal of chromium metal ion solution decreased with the increase in the concentration of chromium solution in case of fruits of *Jatropha gossypifolia* and peel of *Borassus flabellifer*. The percentage removal is between 60-95%. But in the case of *Opuntia Ficus indica* the percentage removal is very high and it ranges between 85-92% which is almost constant at all concentration which shows the efficiency of *Opuntia Ficus indica* in the removal of Chromium solution. Trace amount of latex present in fruits of *Jatropha gossypifolia* acts as precipitating agent and destabilizes the protein solution because of continuous shaking, and then the protein which is destabilized; (colloids) attacks the chromium and sub micro particles are generated. These particles grow under Brownian diffusion process. This process continuously takes place and flocculation occurs. In all these cases, the coagulants used have the destabilizing property and they reduce repulsive forces between the molecules.

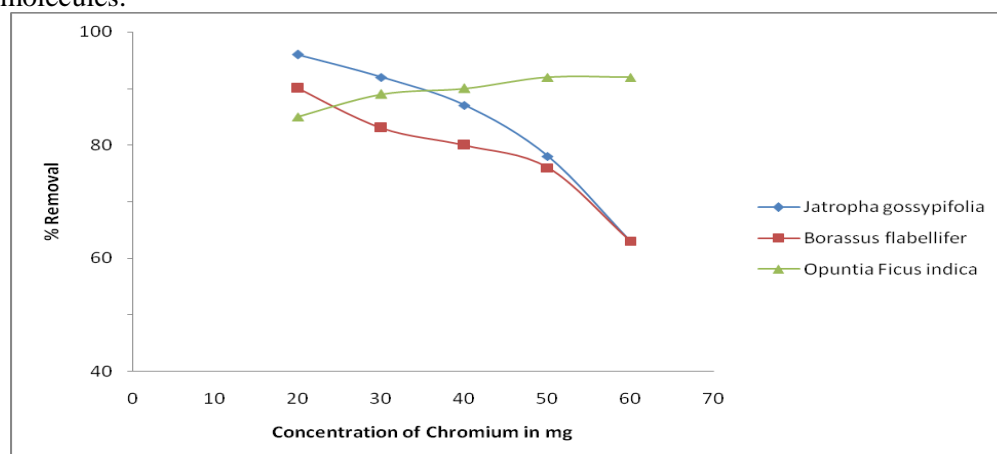


Figure -2: Effect of Chromium metal concentration on coagulant

EFFECT OF PH ON REMOVAL OF CHROMIUM:

To study the effect of pH on coagulation process a constant amount of 1.2 grams of coagulant is added to 15mg L⁻¹ concentrated solution of chromium with different pH. The percentage removal is observed after completion of process by withdrawing samples from each jar and calculated metal concentration using spectrophotometer. From the figure-3 it was observed that the percentage removal is more at higher pH in all the three coagulant. As the pH is raised more negative charges are produced on the colloidal surfaces making them more negative and they are holding chromium (VI) ions. *Opuntia Ficus indica* (Kaur et al., 2012) contains a viscous latex like substance which contains poly electrolyte and its surface bears a negative charge. The poly electrolyte nature of *Opuntia Ficus indica* will cause dissociation and develop a negative charge which attracts the chromium (Cr VI) ions. The present study reveals that flocculation caused by anionic poly electrolyte. This process takes place on the colloidal particles surface of coagulant.

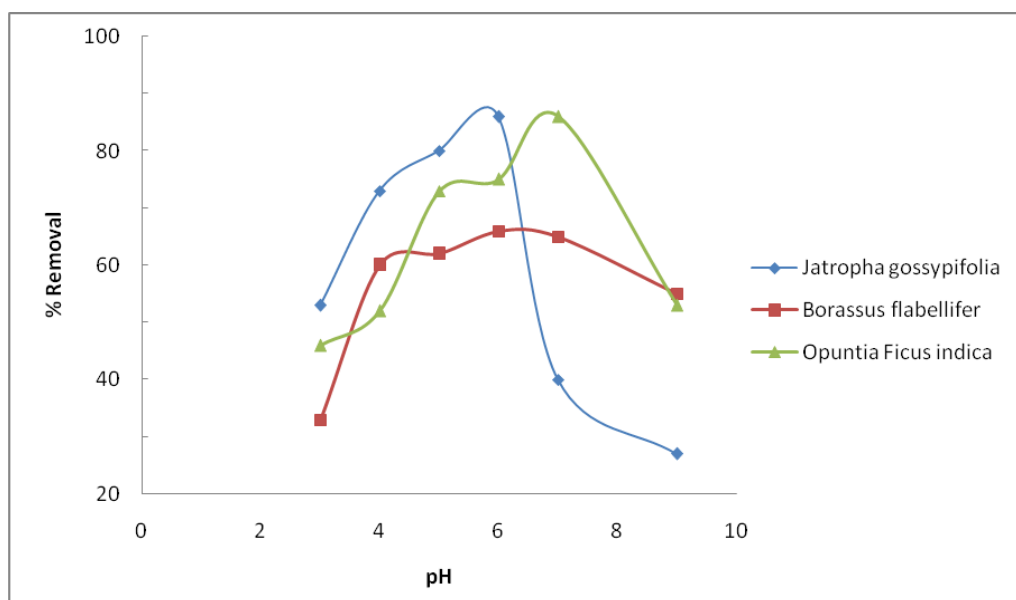


Figure-3: Effect of pH on coagulation

EFFECT OF COAGULANT ON OTHER PARAMETERS OF THE WATER:

The efficiency of coagulants used in present studies are allowed to check the removal capacity of other physical parameters such as pH, Electro conductivity (EC), Turbidity, Salinity, Total Dissolved Solids(TDS), Acidity, Alkalinity and Total Hardness of water. The effect of used coagulants on physical parameters in present experiment is shown in figure- 4(a) and 4(b). From the figure it was observed that there is no change in pH in case of the water treated with fruits of *Opuntia Ficus indica* and peel powder of *Borassus flabellifer*. But change is observed in the water sample which is treated with fruits of *Jatropha gossypifolia*. This change in pH may have been due to the removal of some suspended and dissolved compounds from wastewater. The effect of coagulants on Electro conductivity is very low in case of *Opuntia Ficus indica* and peel powder of *Borassus flabellifer* and efficiency of these two coagulants is 10-12% only. But water treated with fruits of *Jatropha gossypifolia* has shown 53% reduction at constant coagulant dosage that is 1.2 gm L⁻¹. In another study, (Hanif et al., 2008) observed maximum reduction of 77.62% and 88.68% in EC of dyeing and finishing units of textile industry wastewater at a coagulant dose of 1.5g L⁻¹. The Turbidity removal capacity for all used coagulants in this experiment is equal and the percentage of removal is in between 65-70%. Total dissolved solids and salinity is decreased in the water sample which treated with *Jatropha gossypifolia* and reduction of TDS and salinity is 44% and 56%, same of results observed in the study of Hanif et al., (2008) with a maximum reduction of TDS 86.02% and 88.39%, with different coagulants at a constant coagulant dose of 0.5 gm L⁻¹. The removal capacity of Acidity, Alkalinity and total hardness of water is high for all three coagulants used for this study. Alkalinity plays an important role in the removal of some other inorganic contaminants present in wastewater (Bann et al., 2008). From the figure-4(a) and 4(b) it was concluded that used coagulants for the present study has the capacity to remove other water pollutants, after completion of experiment the results were compared with water quality parameters which used for agricultural and aqua cultural growth. The standard values were shown in Table-2 and Table-3 (Pescod et al., 1985; Tatawat and Singh Chandel., 2008; Wilcox., 1948).

Table-1: Effect of coagulant on other physical parameters of water

| S. No | Amount of Coagulant (ml) | Parameter | Before treatment | After Treatment | | |
|-------|--------------------------|------------------------|------------------|-----------------|-----------|---------|
| | | | | J.S | Borasasus | Opuntia |
| 01 | 1.2 | pH | 6.4 | 6.7 | 6.4 | 6.4 |
| 02 | 1.2 | Electro Conductivity | 8.13 | 3.8 | 7.25 | 7.15 |
| 03 | 1.2 | Salinity | 6.5 | 2.9 | 5.7 | 5.5 |
| 04 | 1.2 | Turbidity | 240 NTU | 100 NTU | 90 NTU | 90 NTU |
| 05 | 1.2 | Acidity | 360 | 160 | 60 | 180 |
| 06 | 1.2 | Total Alkalinity | 1440 | 600 | 680 | 700 |
| 07 | 1.2 | Total Hardness | 760 | 216 | 456 | 472 |
| 08 | 1.2 | Total Dissolved solids | 5.26 | 2.93 | 4.7 | 4.65 |

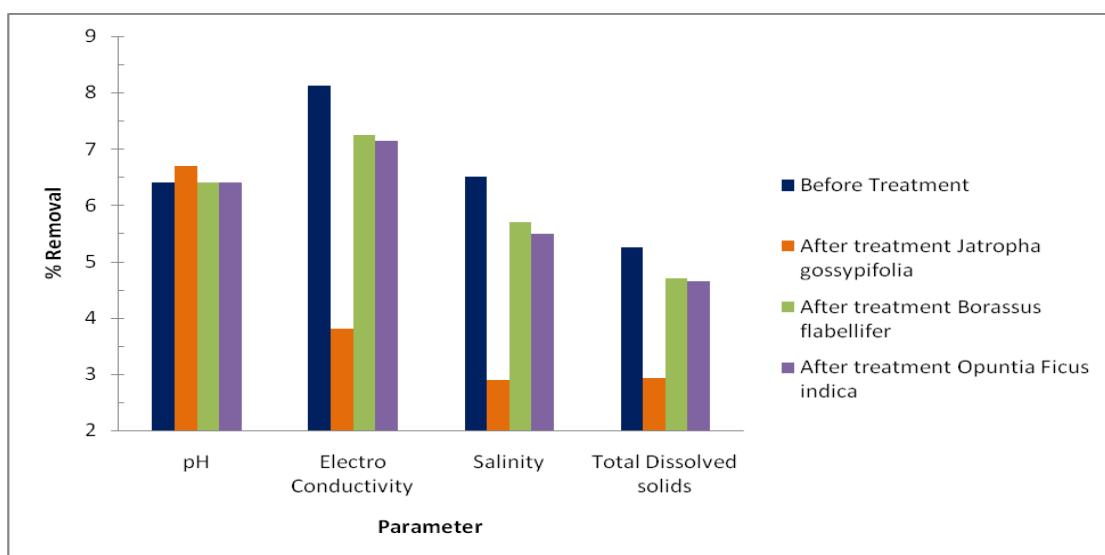


Figure-4 (a): Effect of Coagulant on pH, conductivity, salinity and TDS of water

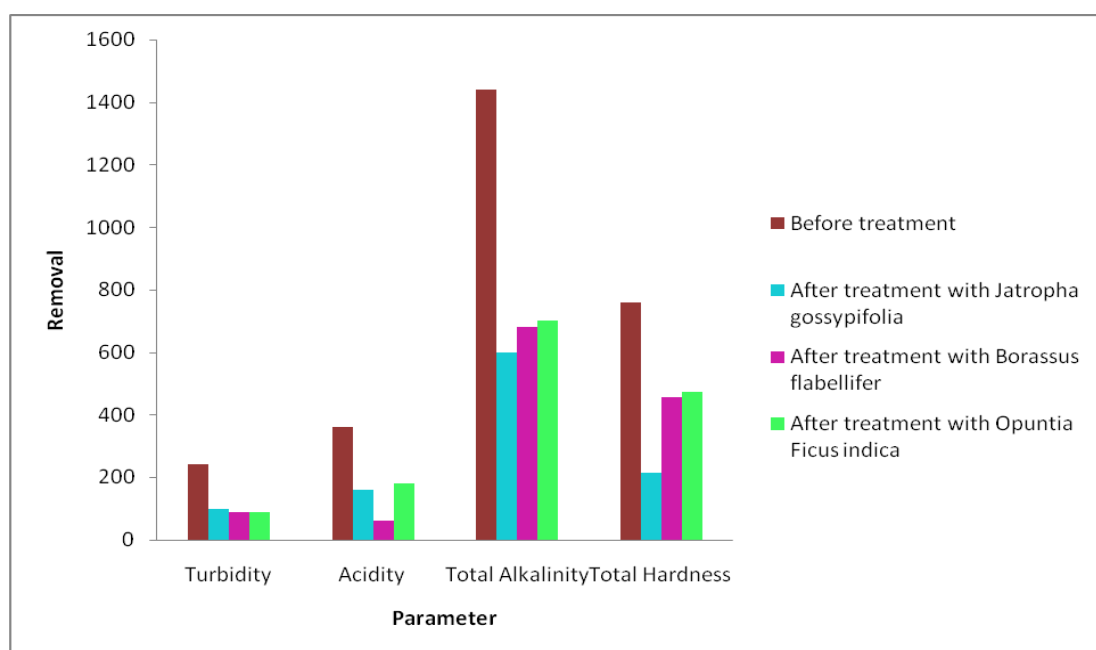


Figure-4 (b): Effect of Coagulant on Turbidity, acidity, alkalinity and hardness of water

Table-2: Water Quality Parameters for Aquaculture use

| S.No | Water parameter | Optimum level |
|------|------------------------|----------------------|
| 01 | Salinity | 10-25 ppt |
| 02 | pH | 6.4-8.5 |
| 03 | Temperature | 26-33 ^o C |
| 04 | Sulphides | <0.03 ppm |
| 05 | Total Ammonia nitrogen | <1.0 ppm |
| 06 | Total Nitrate Nitrogen | <5.0 ppm |
| 07 | Total Hardness | 40-400 ppm |

Table-3: Water Quality Parameters for Agricultural Use

| Parameter | Classification of water | | | | Degree of restriction on use | | |
|--------------|------------------------------|-----------|-------------|------------|------------------------------|----------|--------|
| | Excellent | good | permissible | Unsuitable | None | moderate | Severe |
| EC (dS/m) | <0.25 | 0.25-0.75 | 0.75- 2.25 | 2.25- 5.0 | <0.7 | 0.7-3.0 | >3.0 |
| TDS (mg/Lit) | <200 | 200-500 | 500-1500 | 1500-3000 | <450 | 450-2000 | >2000 |
| pH | Range starts from 6.4 to 8.4 | | | | | | |

From the Table- 2 and 3 (Pescod et al., 1985; Tatawat and Singh Chandel., 2008; Wilcox., 1948) it was observed Electrical conductivity (EC) is the most important parameter in determining the suitability of water for irrigation use and it is a good measurement of salinity hazard to crop as it reflects the TDS in wastewater. So that treated waste water can use for agriculture use and it is mostly suitable for most salt tolerant plants, leaching and drainage are imperative. It is necessary for the environmental researcher to control the water pollution caused by several activities and control the ill effects caused by water pollution for survival of the mankind. So the present study has helped to control the water pollution. Among all the three natural coagulants used in this study fruits of *Jatropha gossypifolia* is very effective in removal of water pollutants compare to other two coagulants used in this study. *Opuntia Ficus indica* is second leading natural coagulant in this experiment. The positive charged chromium metal ions serve to form a bridge among anionic polyelectrolyte and negatively charged functional groups present in fruits of *Opuntia Ficus indica* on the colloidal particle surface. It is characterized as flocculating agents. These are used as natural flocculating agents as covalent bonds in vector compounds or on cell cross linking that are innovative environmentally benign and cost effective (Ambers et al., 2010). Thus, our study proves that the effect of harmful Metal like Chromium can be removed by using naturally available coagulants. Hence, this study provides an economic solution for cleaning up water pollutants and it is recommended to use these coagulants in industries before discharging of waste water which contains chromium. The treated waste water can also suggest using of agriculture and aqua culture (Pescod et al., 1985; Tatawat and Singh Chandel 2008; Wilcox., 1948).

CONCLUSIONS:

It is necessary for an environmental researcher to control ill effects caused by heavy metal pollution in industrial waste waters for survival of mankind, using locally and easily available coagulants. There is a significant improvement in the physicochemical characteristic properties of waste water and heavy metal chromium was successfully controlled by natural coagulants. The coagulants used in the study are plant based poly electrolytes. These poly electrolytes can be effectively used for removal of chromium as they destabilize and reduce repulsive forces between the molecules. The process is bio based and natural technology and it does not generate any non-treatable wastes. These processes are easy to operate and require little or no maintenance. The technology offered by present study is easy to implement and ideal for rural areas. Based on the present research work, other native plants and plant materials should be investigated for removal of not only chromium but other heavy metals and toxic pollutants. The public awareness programmes should be implemented among the rural and urban population. The present research suggests the reusability of treated water for agricultural practices and aqua culture ponds.

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