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Biodegradation and Bio decolorization Of Textile Dye Effluent Using Nanoparticle Synthesized from Hibiscus Cannabinus

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Abstract
Water contamination is a big global problem and some heavy metals in water have caused serious damage to the health of animals and human beings, it is considered to be one of the most serious environmental pollutants. Textile Industries are the largest social and economic perspective in India that discharges tremendous amounts of dye stuff into the water containing recalcitrant compounds, pigments and dye etc. Azo dyes represent the largest production volume of dye chemistry today and their relative importance may even increase in the future. Azo dyes are the most important synthetic colorants which have been widely used in printing, paper manufacturing, etc. The aim of this study is to identify the textile dye degrading efficiency and evaluation of their heavy metals resistant pattern from nanoparticles synthesized Hibiscus cannabinus. The dye effluent samples were collected from in and around Tiruppur, Tamilnadu, South India. The decolorization efficiency of dye was measured using UV-Vis spectrophotometer and the maximum efficiency 92% was obtained on 7th day. The ability of the prepared SNPs for degrading heavy metals ions (Pb^{2+}, Cu^{2+}, Cd^{2+}, Cr^{3+}, Hg^{2+} and Ni^{2+}) from textile dyes was studied and measured using Atomic Absorption Spectrophotometer (AAS). The maximum degrading efficiency of Pb^{2+}, Cu^{2+}, Cd^{2+}, Cr^{3+}, Hg^{2+} and Ni^{2+} were found to be 85.71, 84.56, 90.26, 84.61, 81.81 and 91.42% was obtained on 7th day respectively. Nanoremediation is one of most effective ways to degrade dye stuffs and some heavy metal ions.

Keywords: *Nanoremediation, Azo dyes, Biodegradation, Biodecolorization and Hibiscus cannabinus*

INTRODUCTION

Water pollution is of great concern since water is the prime necessity of life and extremely essential for the survival of all living organisms. Moreover, water pollution is considered to be a major environmental problem worldwide, and among the various water pollutants, heavy metals require special attention because of their toxic effect on humans and the environment [2]. Green fabrication of nanoparticle is clean, non-toxic, eco-friendly, fast and cost-effective as compared to other physico-chemical technologies, which make it a promising technology [24]. Heavy metals are considered to be the most important pollutant in source and treated water [16]. The increased use of heavy metals industrially resulted in an increase in the availability of metallic substances in natural source water [8]. Moreover, heavy metals form a very dangerous category due to their toxic and carcinogenic nature, non-biodegradable and hence, tend to accumulate in the environment for long time. Some of these toxic elements are cadmium, lead, mercury, nickel, chromium and zinc [5]. Nanotechnology can be defined as the science and engineering involved in the design, synthesis, characterization and application of materials and devices whose smallest functional organization in at least one dimension is on the nanometer scale (one-billionth of a meter). In the past few years' nanotechnology has grown by leaps and bounds, and this multidisciplinary scientific field is undergoing explosive development [19]. Nano science and nanotechnologies have a huge potential to bring benefits in areas as diverse as drug development, water decontamination, information and communication technologies, and the production of stronger, lighter materials [11]. An eco-friendly approach for the biogenic synthesis of silver nanoparticles (AgNPs) from an aqueous AgNO3 solution by using the *Hibiscus cannabinus* leaf extract (HCLE) as reducing and stabilizing agent [9]. The silver nanoparticles provide high surface energy, which promotes surface reactivity [12]. Nanoremediation is the use of nanoparticles for environmental remediation [13]. Plant extract based NPs are used in the green synthesis

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processes have received increasing attention for the removal of metal ions [2]. Disposal of dyes into the environment causes serious damage [26]. Trace metals may serious health risks for human even at low concentrations in textile products [24]. The biosynthesized silver nanoparticles were characterized by UV–Visible spectroscopy, Fourier transform infrared spectroscopy, scanning electron microscopy [17]. Industrial effluent is a major source of direct and often continuous input of pollutants into aquatic ecosystems with long-term implications on ecosystem functioning [25]. Effluents discharged from textiles contain a higher amount of metals. These effluents are released on the land as well as discharged into the surface water which ultimately end up in groundwater by leaching and lead to contamination of it due to accumulation of toxic metallic components [18]. Hence, the present study was undertaken to decolorize and degrade the some heavy metal concentrations of textile wastewater.

MATERIALS AND METHOD

Collection of Plant Material

The healthy plant samples of *Hibiscus cannabius leaves* were collected from local area, Manakkal, Trichy. The collected plant materials were transported to the laboratory and shown in Fig.1.

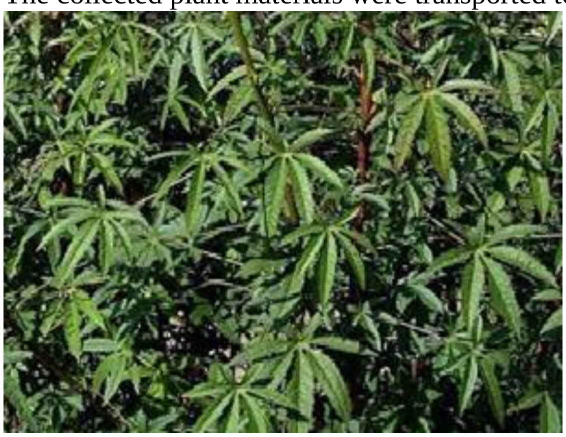

Fig:1 *Fresh Hibiscus cannabius*

Fig:2 *Dried Hibiscus cannabius*

Preparation of Leaf Powder

The *Hibiscus cannabius leaves* were collected, washed and cut into small pieces and dried at room temperature for two weeks and made in to powder for further analysis [2]. The dried leaves were shown in Fig.2.

Preparation of Silver Nanoparticles

To 750ml of millimolar concentration of silver nitrate, 7.5ml of the plant homogenate was added, respectively into a clean conical flask. The conical flasks were then exposed to the sunlight (while being continuously shaken) for the synthesis of the nanoparticles to begin. The colors of the mixture turns from dark green to brown when exposed to sunlight and once it turns to colorless the particles were settled at the bottom of the flasks [9 and 26]. The synthesis of silver nanoparticles was characterized by UV-Visible spectrophotometer, Fourier Transform Infrared Spectroscopy and Scanning Electron Microscope [2 and17].

Photocatalytic Degradation of Dye

Typically textile dye effluent was collected in and around Tiruppur, South India. About 10 mg of biosynthesized silver nanoparticles is added to 100 mL of dye solution. A control was also maintained without addition of silver nanoparticles. Before exposing to irradiation, the reaction suspension was well mixed by being magnetically stirred for 30 min to clearly make the equilibrium of the working solution. Afterwards, the dispersion was put under the sunlight and monitored from morning to evening sunset. At specific time intervals, aliquots of 2-3 mL suspension were filtered and used to evaluate the photocatalytic

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degradation of dye. The absorbance spectrum of the supernatant was subsequently measured using UV-Vis spectrophotometer at the different wavelength. Concentration of dye during degradation was calculated by the absorbance value at 590 nm [7].
Percentage of dye degradation efficiency was estimated by the following formula:

$$\text{Degradation efficiency} = \frac{C_0 - C}{C_0} \times 100\%$$

where C_0 is the initial concentration of dye solution and C is the concentration of dye solution after photocatalytic degradation [22].

Heavy Metal Degradation Efficiency
To identify the initial heavy metal concentration viz. Pb, Cu, Cd, Cr, Hg and Ni in dye effluent was measured by an Atomic Absorption Spectrophotometer (AAS). After decolorizing the dye effluent, the heavy metal concentrations were observed on certain number of cyclic periods. Then the final heavy metal concentrations were measured and compared the values with APHA standards [7].

RESULTS AND DISCUSSION

Physio-chemical parameter of textile dye effluent
The collected sample have been analyzed to determine the physico-chemical parameters like as pH, color, temperature, EC, COD, BOD, TDS, TSS, TS, TKN, Cl, Alkalinity and DO of Textile dye effluent [3].

Table 1: Physio-chemical parameter of textile dye effluent

S.No.	Parameters	Values
1	pH	8.9
2	Colour, Platinum-Cobalt Scale	Pink, 3400
3	Temperature, °C	27.8
4	Electrical Conductivity, ms/Cm	1780
5	COD, mg/l	800
6	BOD, mg/l	160
7	TDS, mg/l	2140
8	TSS, mg/l	1170
9	Total Solids, mg/l	3310
10	TKN, mg/l	350
11	Chloride, mg/l	1495
12	Alkalinity, mg/l	525
13	DO, mg/l	63

Confirmation and Characterization of Silver Nanoparticles (SNPs) Synthesis:

Visual Observation:
In the present study SNPs were synthesized by using leaf extract of *Hibiscus cannabius,* rapidly within 20 min of incubation period and yellowish brown colour was developed by addition of Silver Nitrate. The time duration of change in colour and thickness of the colour varies from plant to plant [2 and 27]. The time taken for the reaction mixture to change colour and the pH was changed from 4.0 to 4.60.

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Table 2: Indication of Color Change in Synthesis of Silver Nano Particle (SNPs)

S.No.	Plant leaf extract + $AgNO_3$	Color change		pH change		Color intensity	Time	Result
	Scientific name	Before	After	Before	After			
1.	***Hibiscus cannabius***	Dark Green	Brown	4.0	4.60	+++	20min	Positive

Color intensity: +++ = very dark colour

Fig 3: Indication of Color Change in synthesized AgNPs from *Hibiscus Cannabius*

Fig 4 (a)

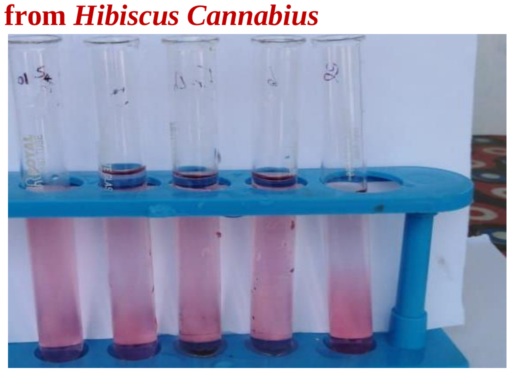

Fig 4 (b)

Fig 4 (a): Dye Degrading Efficiency of nanoparticle from *Hibiscus cannabinus* at Initial day
Fig 4 (b): Dye Degrading Efficiency of nanoparticle from *Hibiscus cannabinus* at 5th day

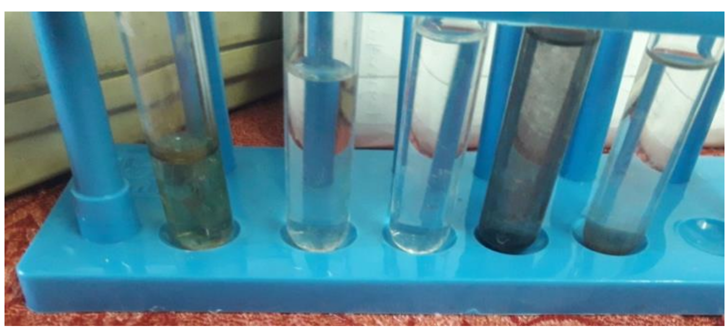

Fig 4 (c)

Fig 4 (c): Dye Degrading Efficiency of nanoparticle from *Hibiscus cannabinus* at 7th day

Photocatalytic Degradation of Textile Dye Effluent

The release of dye effluents from textile industry is a major source of water pollution. Dye is one of pollutant of wastewater and has potential threat to the environment [4 and 6]. In the current investigation, fabric azo dyes were collected from Tiruppur, Tamilnadu, South India, and decolorized by silver nano particle isolated from plant extract under solar light. Dye degradation was initially identified by color change [12]. Initially,

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the colour of dye shows deep pink color changed into light pink after the 1h of incubation with silver nanoparticles while exposed to solar light (Fig 4a). The degradation was analyzed UV-Vis Spectrophotometry. We studied the degradation of wastewater containing textile dye, using green synthesized AgNPs as catalysts. Thus the catalytic activity of the silver nanoparticles was found to depend on the particle size and its shape [14]. Photocatalytic degradation of dye was investigated by biosynthesized (*Hibiscus cannabinus)* AgNPs with solar irradiation technique by biometrically at different time intervals as shown in Fig 4b**.** The characteristic absorption peak of dye solution was found to be 590 nm. Degradation of dye was visualized by decrease in peak intensity within 6 h of incubation time. There is no considerable shift in peak position for dye solution without exposure to biosynthesized AgNPs of samples. Visible light was found to be faster in decolorizing dyes in the presence of metal catalyst [24]. The adsorption of AgNPs on to the dye solution was initially low and further increased with constant increase in time. The variation in the absorption intensity at 590 nm for dye samples signifying the faster reaction rate. The degradation of the dyes increases with decrease in the size of the particles. The reducing in the structure of the metal particles favors the proliferation in the amount of the coordinate atoms and improves the adsorption of molecules on the surface of catalysts and thus improves the degradation of dyes. Thus the catalytic activity of the silver nanoparticles was found to depend on the particle size and its shape.

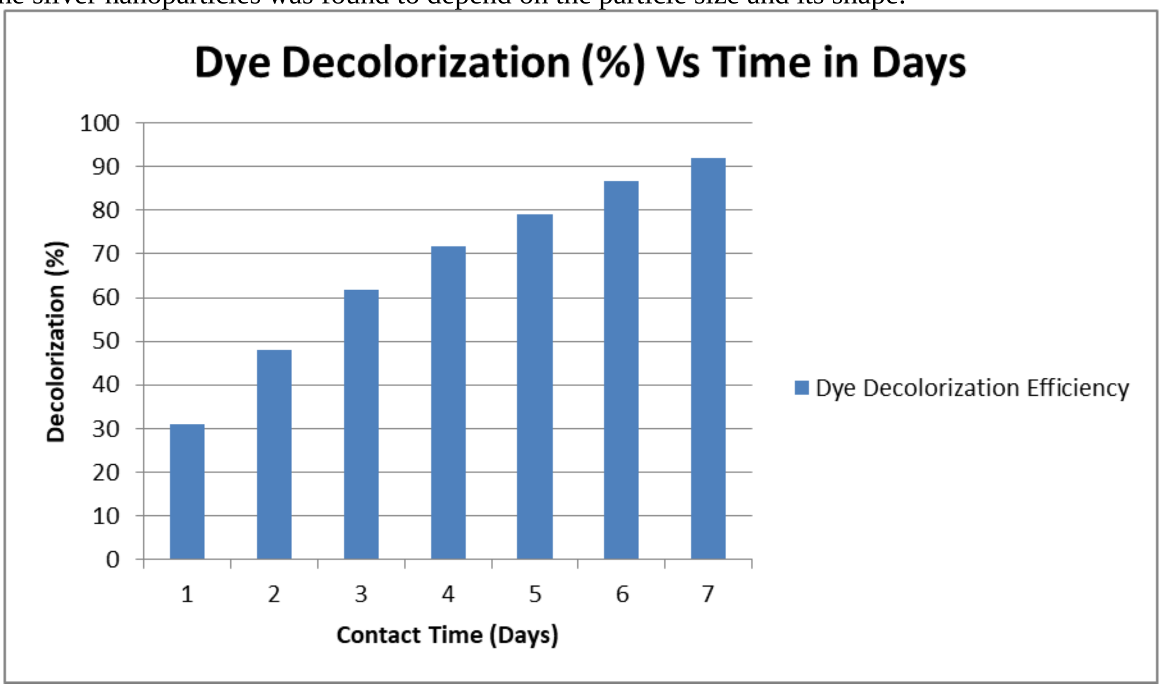

Fig 5: Contact Time in days with respect to % Dye Removal Efficiency

The photocatalytic degradation efficiency was observed on the regular intervals (Day 1 to Day7). Biodecolorization efficiency was measured by UV-Vis Spectroscopy [17]. On the 3rd day achieves the 62% degradation of textile dyes and the same process it was found that the maximum biodecolorization efficiency 92% obtained on the 7th day. After 7th day the color itself remain same. Finally the photocatalytic degradation efficiency of dye effluent at day 1 to 7 was obtained at 31, 48, 62, 72, 79, 86 and 92%, respectively as shown in Fig 5.

Initial heavy metals concentrations in textile dye effluent

Fig. 6 shows the initial heavy metals concentrations of textile dye effluent. The concentrations for lead, copper, cadmium, chromium, mercury and nickel are 0.63, 0.285, 0.411, 0.26, 0.11 and 0.35 mg/L, respectively.

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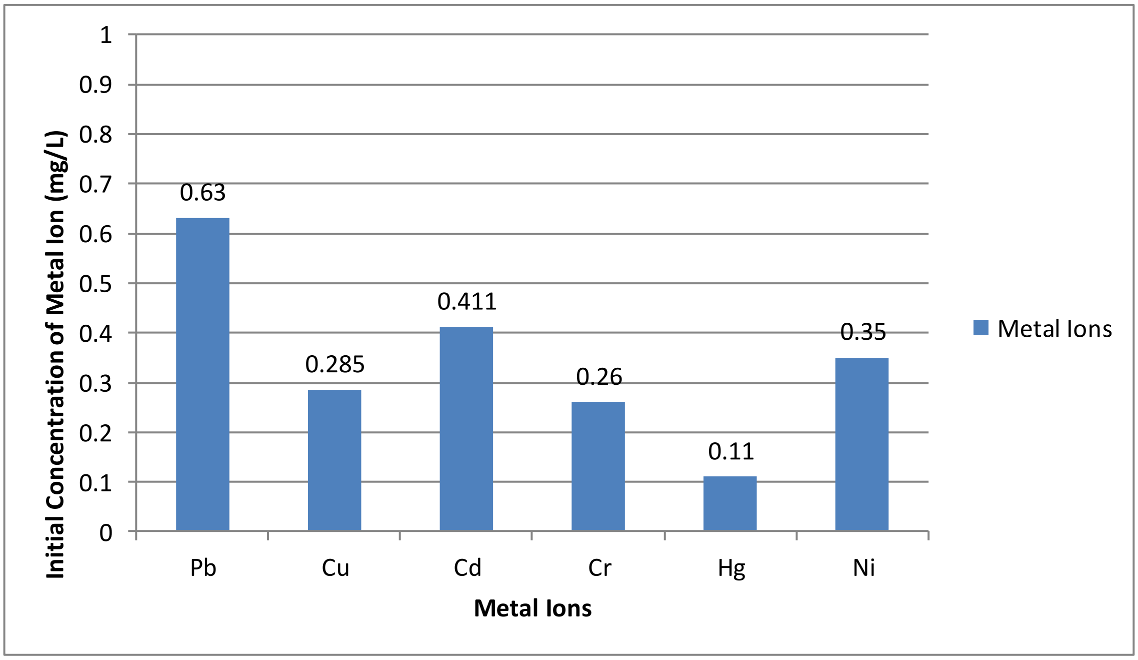

Fig 6: Initial concentration of metals ion (mg/L) in Dye Effluent

The initial concentration of Lead (Pb) in dye effluent is highest because the influent from the production process discharged contained high levels of Lead (Pb) and low levels of Mercury (Hg) on the sampling day. In complex metal dyes, the metal is responsible to form a chemical bond with the organic or azo or reactive dye molecule. Thus, it is an indispensable constituent of the textile dye and governs the fastness absorb the colours. The silver nano synthesized *Hibiscus cannabinus* was used to biodegrade the heavy metal ions [9] and comparing the APHA standards.

Lead (Pb)

Lead has been linked to skin irritation, abdominal cramps, nausea, convulsions, lead poisoning, cancer, and death in the most serious cases [7]. Fig. 6 shows the Lead (Pb) with an initial concentration of 0.63 mg/L. The reduction of final concentrations of lead was observed after decolorization on the 7th day was 0.09 mg/L and the degradation efficiency was analytically calculated to found 86% biodegradation efficiency. Therefore, it can be observed that the final concentration of Pb value is within acceptable limits.

Copper (Cu)

Copper on a regular basis can cause liver damage, abdominal pain, cramps, nausea, diarrhea, and vomiting. The initial Copper (Cu) ion concentration was measured by Atomic Absorption Spectrometry (AAS) of 0.285 mg/L [11 and 21]. The reduction of final concentrations of copper was observed after decolorization on the 7th day was 0.044mg/L and the degradation efficiency was analytically calculated to found 84% biodegradation efficiency. Therefore, it can be observed that the final concentration of Cu value is within acceptable limits and comparing to lead it was less biodegradation (Cu<Pb).

Cadmium (Cd)

Cadmium dyes have been partially replaced by azo dyes. Low levels exposure to Cd may lead to damage to the kidneys, liver, skeletal system, and cardiovascular system, as well as to deterioration of sight and hearing. The Cadmium (Cd) in the textile dye effluent is 0.411 mg/L and measured by the instrument AAS [23]. After photocatalytic degradation of dye stuffs on 7th day, the cadmium metal final concentration was 0.04 mg/L. Nearly it was greatly reducing the concentration of heavy metal ion upto 10 times comparing the initial values. The biodegradation efficiency was found to be 90%, but the reduction of cadmium ion

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was exceeding the acceptable limits and comparing to lead and copper the biodegradation efficiency was more but not in tolerable range (Cu<Pb<Cd).

Chromium (Cr)

Chromium is very toxic by inhalation and dermal route and causes lung cancer, nasal irritation, nasal ulcer and hypersensitivity reactions like contact dermatitis and asthma [8 and 10]. The Chromium ion was found to be Cr^{3+} and Cr^{6+}. From that the total chromium ion concentration were studied [19]. The initial concentration of chromium was shown in Fig 6, is 0.285mg/L. The maximum decolorizing the textile dye was observed on 7th day of incubation and the biodegradation efficiency of Cr is 85% and the final concentration is 0.04 mg/L. As per APHA standards [18] the biodegradation of chromium was in acceptable range and comparing the previous metals (Cu<Cr<Pb<Cd).

Mercury (Hg)

The initial Hg ion was found to be 0.11 mg/L, it was the least value comparing other initial metal ion concentration. After biodegradation, the Hg value was observed 0.02 mg/L. Comparing with the acceptable limits it was too more, if the mercury value is high it leads to cause neurological and behavioral disorders, such as tremors, emotional instability, insomnia, memory loss, neuromuscular changes and headaches. They can also harm the kidneys and thyroid. The biodegradation efficiency was found to be 81%, but the reduction of Hg ion was exceeding the acceptable limits (APHA Standards) [24] and comparing to lead, copper, Cadmium and Chromium the biodegradation efficiency was in increasing order (Hg<Cu<Cr<Pb<Cd).

Nickel (Ni)

The nickel ion compounds can be carcinogenic to humans when directly ingested or inhaled in very high doses [16]. The initial concentration of Ni was 0.35 mg/L and it can be reduced to 0.03mg/L. The biodegradation efficiency was found to be 91% on 7th day. Comparing to previous heavy metal ions it can be highly biodegraded and the removal efficiency in increasing order (Hg<Cu<Cr<Pb<Cd<Ni)

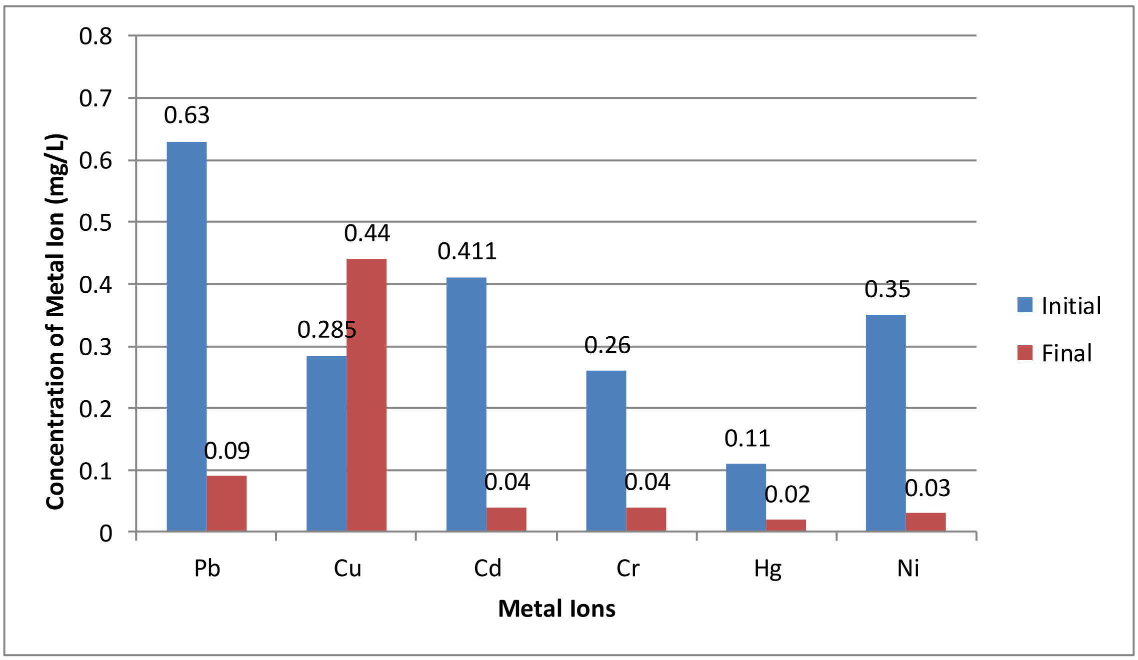

Fig 7: Percentage of Heavy metals Biodegraded using *Hibiscus cannabinus*

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From Fig 7 describes the graphical representation of initial and final heavy metal concentration and Fig 8 shows the heavy metal degradation efficiency with respect to time, the maximum biodegrading efficiency 91.42 % was estimated as Nickel (Ni^{2+}) ion.

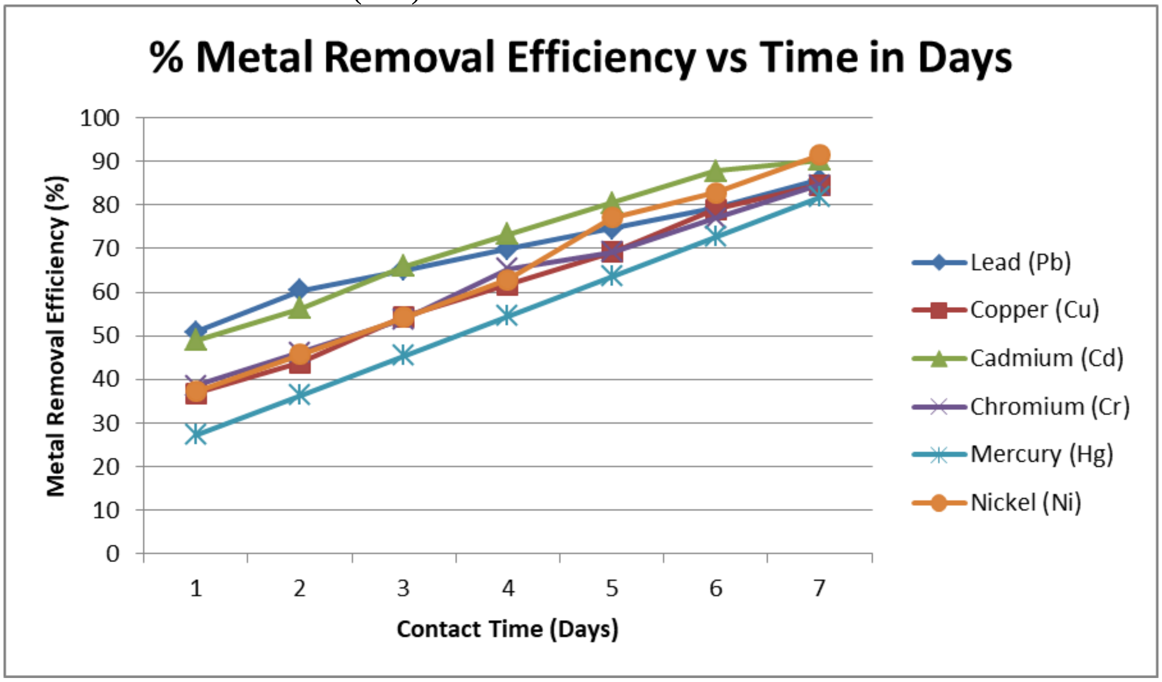

Fig 8: Contact Time with respect to Metal Removal Efficiency

SUMMARY AND CONCLUSION

The biodegradation efficiency of heavy metals from textile dye effluent is effective using nano synthesized *Hibiscus cannabius*. The photocatalytic degradation of dye effluent and biodegradation of heavy metals from textile dye effluent is high whereby the percentage of removal is more than 80 percent of the initial concentration. The biosynthesized AgNPs exhibits a very high degradation activity under visible light source.

The photocatalytic biodecolorization efficiency of dye effluent at day 1 to 7 was obtained at 31, 48, 62, 72, 79, 86 and 92%. On the 7th day of degradation the maximum decolorization efficiency was achieved. The ability of the prepared AgNPs for degrading heavy metals ions (Pb^{2+}, Cu^{2+}, Cd^{2+}, Cr^{3+}, Hg^{2+} and Ni^{2+}) from textile dyes was studied and maximum degrading efficiency of each metal ions are estimated, such as Lead, Copper, Cadmium, Chromium, Mercury and Nickel were found to be 85.71,84.56, 90.26, 84.61, 81.81 and 91.42 %, was obtained on 7th day respectively. The Pb, Cu, Cr and Ni are in acceptable ranges comparing APHA standards.

The present study, it is found that the use of natural renewable and eco-friendly reducing agent used for synthesis of silver nanoparticles exhibits excellent photocatalytic activity against dye molecules and degrade heavy metals in water purification systems and dye effluent treatment.

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