Journal of ENVIRONMENTAL Treatment Techniques

J. Environ. Treat. Tech.
ISSN: 2309-1185
Journal web link: http://www.jett.dormaj.com

Synthesis of Silver Nanoparticles from Fish Scale Extract of *Cyprinus carpio* and its Decolorization Activity of Textile Dyes

Bharathi Vadivelu[1], Arun Meyyazhagan[2], Sampathkumar Palanisamy[3], Vijaya Anand Arumugam[4*], Hesam Kamyab[5*], Balamuralikrishnan Balasubramanian[6], Shreeshivadasan Chelliapan[5], Krishna Kumar Yadav[7]

[1]Biological and Bioinformatics Research Centre, Trichy, Tamil Nadu, India
[2]EuroEspes Biomedical Research Centre, Institute of Medical Science and Genomic Medicine, Corunna, Spain
[3]Department of Chemistry and Biosciences, SASTRA Deemed University, Kumbakonum, Tamil Nadu, India
[4]Department of Human Genetics and Molecular Biology, Bharathiar University, Coimbatore, Tamil Nadu, India
[5]Engineering Department, Razak Faculty of Technology and Informatics ,Universiti Teknologi Malaysia Jalan sultan Yahya Petra 56100 Kuala Lumpur, Malaysia
[6]Department of Food Science and Biotechnology, College of Life Sciences, Sejong University, Seoul, South Korea
[7]Institute of Environment and Development Studies, Bundelkhand University, Jhansi, 284128, India

Received: 10/01/2020 Accepted: 11/05/2020 Published: 20/09/2020

Abstract

There is an increasing commercial demand for nanoparticles due to their wide applicability in various areas such as electronics, catalysis, chemistry, energy, and medicine. This work deals with the synthesis and characterization of silver nanoparticles (AgNPs) using *Cyprinus carpio* fish scale extract to de-colorization of textile dyes. The synthesized nanoparticles were characterized by using UV-Vis absorption spectroscopy, FT-IR and SEM analysis. The reaction mixture turned to a brownish gray color after 5 hrs of incubation and exhibits an absorbance peak around 450 nm characteristic of AgNPs. The SEM analysis showed AgNPs were pure and polydisperse and the size were ranging from 200 nm. The approach of biosynthesis seems to be cost efficient, ecofriendly and easy alternative to conventional methods of AgNPs synthesis. Dye degrading efficiency of AgNPs was assayed against azo dyes. At the end of 24 hrs AgNPs showed 48.38% of degradation. As the days of incubation increases from 1 day to 7 days, the degradation efficiency was also increased from 48.38% to 93.54% at the end of 7th day of incubation. Further, the FT-IR results confirmed that, the complex, toxic azo dyes are degraded into simple, non-toxic compounds.

Keywords: Fish scale, *Cyprinus carpio*, Silver nanoparticle, Textile dye, Decolorization

1 Introduction

Common carp (*Cyprinus carpio*) is considered to be a very important aquaculture species in many Asian and some European countries. *C. carpio* is an exotic fish species in India. The *C. carpio* is usually considered to be one of the most ecologically damaging fish species of all freshwater bodies. The synthesis of silver nanoparticles (AgNPs) is extensively studied by using biological methods, but the development of reliable technology to produce nanoparticles is an important aspect of nanotechnology. Their capability to reach high biomass and their feeding nature has been occupied in causing major environmental poverty in several freshwater ecosystems. The AgNPs are between 1 nm and 100 nm in size has many applications due to a large degree of commercialization. It is an attractive material for its distinctive properties, such as good conductivity, chemical stability [1-3].

Textile dyes are complex unsaturated aromatic compound that possesses characters like intensive color formation, solubility, and fastness (fading property). In the early days, dyes were used which was produced from natural sources. Azo dyes are the most important group of synthetic colorants characterized by the presence of one or more azo group (-N=N-). They are the most versatile class of dyes and constitute 60% of the dyes annually produced [4]. The effluents from textile industries are complex, containing a wide variety of dyes and other products, such as dispersants, acids, bases, salts, detergents, humectants, oxidants, etc. Discharge of these colored

Corresponding authors: (a) Vijaya Anand Arumugam, Department of Human Genetics and Molecular Biology, Bharathiar University, Coimbatore, Tamil Nadu, India. E-mail: avamiet@yahoo.com. (b) Dr. Hesam Kamyab, Engineering Department, Razak Faculty of Technology and Informatics ,Universiti Teknologi Malaysia Jalan sultan Yahya Petra 56100 Kuala Lumpur. E-mail: hesam_kamyab@yahoo.com.

effluents into rivers and lakes results in reduced dissolved oxygen concentration, thus creating anoxic conditions that are lethal to resident organisms. The mechanism of microbial degradation of azo dyes involves the reductive cleavage of azo bonds (-N=N-) with the help of azo reductase under anaerobic conditions involves a transfer of four-electrons (reducing equivalents), which proceeds through two stages at the azo linkage and in each stage two electrons are transferred to the azo dye, which acts as a final electron. The resulting intermediate metabolites (e.g., aromatic amines) are further degraded aerobically or anaerobically. Thus, in the presence of oxygen usually inhibits the azo bond reduction activity since aerobic respiration may dominate utilization of NADH; thus impeding the electron transfer from NADH to azo bonds. The potential toxicity, mutagenicity, and carcinogenicity of such compounds are well documented and have been reviewed elsewhere [5]. Therefore, the aim of this study synthesis and characterization of AgNPs from *C. carpio* fish scale extracts and to evaluate the activity on de-colorization of textile dyes.

2 Materials and Methods

2.1 Synthesis of silver nanoparticles

The fish scale sample collected from *C. carpio*. The fish scale samples are sun dried for 3 days, grind the sample and used for the synthesis of AgNPs. To take 10g of fish scale powder was mixed with 100ml of distilled water, then boiled water bath at 70ºC in 20 minutes. After cooling few minutes, to filter by using Whattman filter paper get the fish scale extract. After, prepared 100ml of silver nitrate solution. Added the scale extract + silver nitrate solution (1:9) ratio. Incubate at dark condition for 72 hrs. After, 3 days color changing of reddish-brown color sedimentation formed (AgNPs).

2.2 Characterizarion of silver nanoparticles

After the synthesis of AgNPs, the synthesized AgNPs are taken for centrifugation at 6000 rpm for 15 mines. After centrifugation the supernatant and pellet were collected. The pellet was re-dispersed in deionized water to get uncoordinated biological molecules. The supernatant was collected and stored in refrigerator for further use. The pellet is airs dried for 24 hours and powdered from AgNPs are taken into Eppendorf tube to undergo SEM analysis. The FT-IR Spectra of the sample were recorded in order to Characterization the presence of functional groups in isolated stains. All the measurements were carried out in the range of 100-1000.

2.3 Photocatalytic degradation of dye

Typically, Azo dye was added to 1000 mL of double distilled water used as a stock solution. About 10 mg of biosynthesized AgNPs was added to 100 mL of Azo dye solution. A control was also maintained without the addition of AgNPs. 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 was filtered and used to evaluate the photocatalytic 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 [6].

3 Results and Discussion

The present study was carried out of preparation of AgNPs from the fish scale extract of *C. carpio*. We developed a simple protocol for synthesis and characterization of AgNPs from the fish scale extract of *C. carpio* and studied the presents of bioactive compounds. About 10% of the fish scale extracts were mixed with silver nitrate solution in 1:9 proportions and kept at room temperature for 72 hrs for the development of reddish-brown color (Table 1). But in our investigation, the AgNPs usually exhibited reddish brown color in aqueous solution, due to excitation of surface plasmon resonance in the AgNPs after incubation [7]. The appearance of reddish-brown color in the reaction vessels suggested the formation of AgNPs. Silver nitrate is used as reducing agents as silver has an identical property such as good conductivity, catalytic and chemical stability.

Table 1: Indication of Color Change for synthesis of AgNPs

Extract	Color change		pH Change		Color intensity	Time	Result
	Before	After	Before	After			
Fish scale Extract+AgNo3	Light Yellow	Brown	6	7	+++	20 Min	Positive

The reduction of silver metal ions to AgNPs was preliminarily analyzed using UV-Vis Spectrophotometer between 200-1000nm (Table 2 and Fig. 1). This analysis showed an absorbance peak at 218 nm which was specific for Ag nanoparticles. The reaction mixture changes the color by adding various concentrations of metal ions. These color changes arise because of the excitation of surface plasma vibrations in the AgNPs.

Table 2: Represents the corresponding UV-VIS absorption spectrum of AgNPs

Wavelength	Absorbance
218.05	4.0000
751.55	0.2371
937.20	0.2581

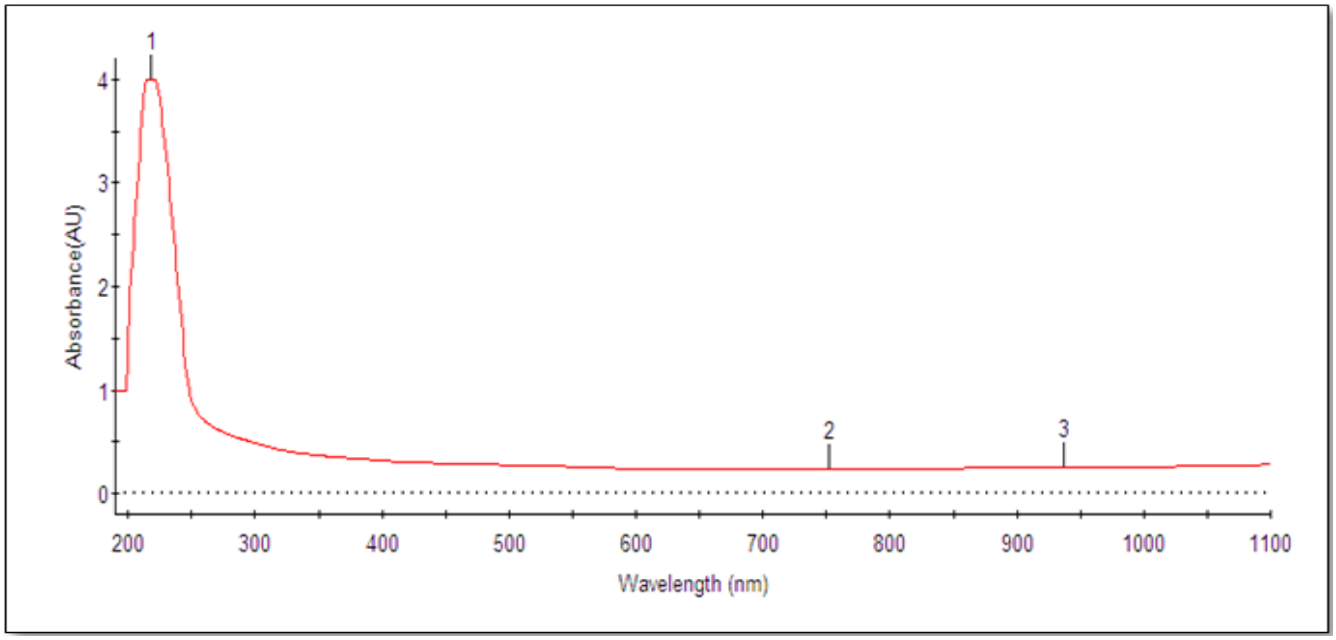

Figure 1: Represents the corresponding UV-VIS absorption spectrum of AgNPs recorded (1:9)

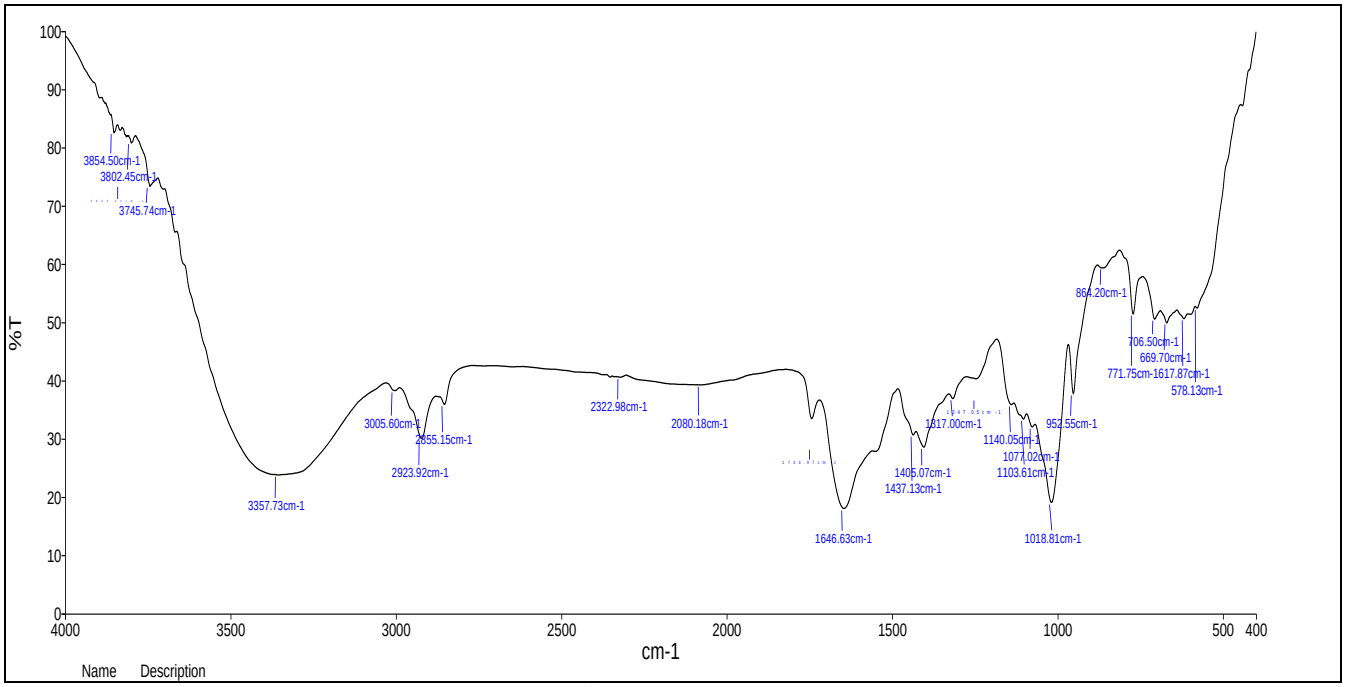

Figure 2: FT-IR analysis spectra of AgNPs showed various transmission peats (1:9) ratio

It shows yellowish to dark brown in color. The dark brown color of silver colloid is accepted to surface plasma resonance (SPR) arising due to the group of free conduction electrons induced by an interacting electromagnetic field. The FT-IR spectra show the biosynthesized AgNPs and carried out to possible interactions between protein and AgNPs. The result of FT-IR analysis of SNP is presented in Fig. 2 spectra of AgNPs showed transmission peaks at 3854.50 cm^{-1}, 3357.73 cm^{-1}, and 3005.60 cm^{-1}, 2923.92 cm^{-1}, 1646.63 cm^{-1}, 771.75cm^{-1}, 669.70 $cm^{-1}$and 578.13 cm^{-1} respectively (Table 3 and Fig. 2). Fig. 3 showed that the AgNPs are spherical, triangular, rectangular and cubical in shape with uniform distribution. However, no most occasions; agglomeration of the particles was observed probably due to the presence of the weak capping agent which moderately stabilized the nanoparticles. Also, reveals the presences of agglomerated nanoparticles were in the range 150.72 -200.49 nm; however, the average size of an individual particle is estimated to be 200nm (Fig. 3).

Table 3: Compound group and frequencies (1:9) ratio

Group frequency (cm $^{-1}$)	Functional group
3854.50 cm^{-1}	Primary amines
3357.73 cm^{-1}	Carbonyl group (open-chain acid anhydride)
3005.60cm^{-1}	Amide Group
2923.92 cm^{-1}	Trimethyl
1646.63 cm^{-1}	Methyl C-H Group
771.75cm^{-1}	Disulfides
669.70 cm^{-1}	Disulfides
578.13 cm^{-1}	Aryl disulfides

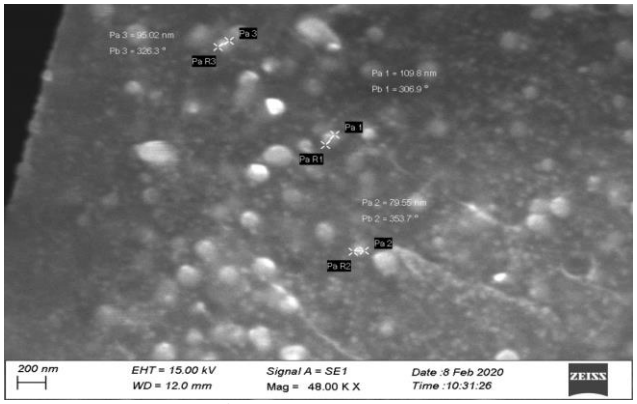

Figure 3: SEM of synthesized (1:9) silver nanoparticles

The SEM images show AgNPs were spherical and polydisperse. Immobilization of Ag NPs on polymer films using fish scale extract and was characterized by UV-Vis spectroscopy, FT-IR and SEM. Recently, both academic and industrial research has explored the possibility of using AgNPs as a next generation anticancer therapeutic agent, due to the conventional side effects of chemo and radiation therapy. Although AgNPs play an important role in clinical research, several factors need to be considered, including source of raw materials, the method of production, stability, bio distribution, controlled release, and finally toxicological issues of human beings. We report a simple, facile, inexpensive, eco-friendly and green synthesis of AgNPs from the fish scale extract without employing man-made chemicals. The UV-Vis spectroscopy and FT-IR analysis is confirmed the preliminary confirmation of the formation of AgNPs. SEM image showed the spherical shape with an average particle size of 200 nm. The biosynthesized AgNPs from the fish scale extract of *C. carpio* showed promising dye degrading efficiency. Dye degrading efficiency of AgNPs isolated from plant extract was assayed against azo dye. At the end of 24 hrs nanoparticles of the fish scale extract showed 48.38% of degradation. As the days of incubation increases from 1 day to 7 days, the degradation efficiency was also increased from i.e. 48.38% to 93.54% at the end of 7th day of incubation. The FT-IR results confirmed that, the complex, toxic azo dyes are degraded into simple, non toxic compounds.

In the current investigation, fabric azo dyes were collected from Tiruppur, Tamilnadu, South India, and decolorized by AgNPs isolated from *C. carpio* under solar light. Dye degradation was initially identified by color change. Initially, the color of dye shows deep pink color changed into light pink after the 1h of incubation with AgNPs while exposed to solar light**.** The degradation was analyzed spectrophotometrically. At every 24 hrs intervals sample was derived and analyzed spectrophotometrically. The control showed 0.31 Optical Density (OD). At the end of 24 hrs 48.38% of degradation. As the days of incubation increases from 1 day to 7 days, the degradation efficiency was also increased from i.e. 48.38% to 93.54% at the end of 7th day of incubation (Table 4 and Fig. 4).

Table 4: Dye degradation efficiency of synthesized silver nanoparticles

Days of Incubation	Initial (OD)	Absorbance after photocatalytic degradation (590 nm)	Degradation efficiency (%)
1	0.31	0.16	48.38
2	0.31	0.13	58.06
3	0.31	0.08	74.19
4	0.31	0.07	77.41
5	0.31	0.05	83.87
6	0.31	0.03	90.32
7	0.31	0.02	93.54

During degradation the catalysis was occurring on the surface region of metals, therefore increasing the surface area availability will significantly improve the efficiency of the catalyst. Decreasing the particle size will increase the catalytic activity, but there is a critical size below which proves that further decreases will actually hamper the reaction. Metal nanoparticles support the electron (e-) relay from the donor to the acceptor and act as a substrate for the e- transfer reaction. During an e-transfer reaction, the reactants are adsorbed on the surface of the metal and consequently, the reactants gain an e- and are reduced. Thus, AgNPs act as an efficient catalyst through the electron transfer process in all the above catalytic reactions [8]. Table 5 and Table 6 showed the FT-IR spectrum of control and samples obtained after decolorization of both dyes showed various peaks. The appearance of some new peaks and absence of important peaks in incubation with AgNPs while exposed to solar light of the dyes have been observed in the FT-IR analysis of the metabolites produced after decolorization. A new peak at 1384 cm^{-1} represented -N=N- stretching vibration. The C-H deformation showed at 1112 cm^{-1}. The peak at 1384 cm^{-1} showed N-H stretching vibration. The significant change in the FT-IR spectrum of metabolites compared to control spectrum suggests the biotransformation of complex dyes present in the mixture into simple form. The FT-IR spectrum of control dye 6 displays peaks at 3449 for intramolecular hydrogen bonding and O-H stretches. Peaks in the control dye spectrum represented symmetric stretching at 1384 cm^{-1} and asymmetric stretching at 1114 cm^{-1} for C-N. C-N stretching at 1637 cm^{-1} represented nature of the aromatic amine group present in parent dye; 3449 cm^{-1} and 2075 cm^{-1} represented the presence of a free NH group of parent dye. Whereas peak at 1637 cm^{-1} represented -N=N- stretching of azo group. In degraded extracted metabolites, a new peak at 435 cm^{-1}

represented C-H deformation of alicyclic CH_2 whereas a peak at 685 cm^{-1} was observed for substituting anilines. The FT-IR analysis result of peak at 3375.38 cm^{-1} indicates primary amides, the peaks at 1789.9 cm^{-1} indicates carbonyl Group, the peaks at 1639.78 cm^{-1} indicates amide Group.

Table 5: The FT-IR spectrum of control dyes

FREQUENCY RANGE	TYPE OF BOND	TYPE AND GROUP
3459	O-H Stretch- H Bonded	Alcohols, phenols
2080	-C=C- Stretch	Alkynes
1638	N-H bend	1º amines
1384	C-H bend	Alkanes
685	C - Br Stretch	Alkyl halides

Table 6: The FT-IR spectrum of samples obtained after decolorization of dyes

FREQUENCY RANGE	TYPE OF BOND	TYPE AND GROUP
3449	O-H Stretch-H Bonded	Alcohols, phenols
2075	-C=C- Stretch	Alkynes
1638	N-H bend	1º amines
667	C - Br Stretch	Alkyl halides

4 Conclusion

To conclude, this is an efficient, eco-friendly and simple process. The nanoparticles were found to be active in degrading azo dye solution with visible light illumination. These findings suggest that AgNPs synthesized by facile method from plant extract are able to degrade dyes in the presence of visible light and pave way for ecological health and environmental bioremediation. Similarly, instead of using hazardous, time consuming and costly chemicals, we could protect our environment from dyes by using these types of natural AgNPs isolated from fish extract. The present study, it is found that the use of natural, renewable, and eco-friendly, reducing agent used for synthesis of AgNPs exhibits excellent photocatalytic activity against dye molecules and can be used in water purification systems and dye effluent treatment.

Acknowledgment

This research work was acknowledged by Universiti Teknologi Malaysia under the Research University Grant, Vote Number: Q. K130000.2510.13H11. Hesam Kamyab is a researcher of Universiti Teknologi Malaysia (UTM) under the Post-Doctoral Fellowship Scheme (PDRU Grant) for the project: “Alternative Innovation of Enhancement Technologies for Algal Oil Extraction” (Vote No. Q. J130000.21A2.03E31) and Enhancing the Lipid Growth in Algae Cultivation for Biodiesel Production.

References

1. Balon, EK. Origin and domestication of the wild carp, *Cyprinus carpio*: from Roman gourmets to the swimming flowers. *Aquaculture*. 1995;129(1-4):p. 3-48.

2. Gong P, Li H, He X, Wang K, Hu J, Tan W, Zhang S, Yang X. Preparation and antibacterial activity of Fe_3O Ag nanoparticles. *Nanotechnology*. 2007;18:p. 604-611.

3. Aminiranjbar GH. Heavy metal concentration in surficial sediments from Anzali wetland, Iran. *Journal of Water Air and Soil Pollution*. 1998;104 (4):p. 305-312.

4. Russ R, Rau J, Stolz A. The function of cytoplasmic flavin reductases in the reduction of azo dye. *Int. J Chem*. 2000;66(4):p.1429-34.

5. Chung KT, Cerniglia CE. Mutagenicity of azo dyes: structure- activity relationships. *Mutation Res*. 1992; 277(3):p.201-220.

6. Guzman MG, Dille J, Godet S. Synthesis of silver nanoparticles by chemical reduction method and their antibacterial activity. *World Acad. Sci. Eng. Technol*. 2008;43:p.357-364.

7. Karcher S, Kornmuller A, Jekel M. Screening of commercial sorbents for the removal of reactive dyes. *Dye and Pigment*. 2001; 51:p.111-125.

8. Duran N, Marcato PD, Conti RD, Alves OL, Costa FTM, Brocchi M. Potential use of silver nanoparticles on pathogenic bacteria, their toxicity and possible mechanisms of action, *J. Braz. Chem. Soc*. 2010; 21(6):p.949-959.