Methylene blue degradation using highly electro catalytic silver nanoparticles

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Abstract

In this study, silver nanoparticles were used to remove methylene blue dye in aqueous solution. The silver nanoparticles subjected to UV-Visible spectroscopy, Particle Size Analysis, Zeta Potential and Fourier Transform Infrared Spectroscopy. The absorbance peak obtained around 420 nm, which showed that the samples are active and contain silver nanoparticles. The sample is in nano range with 47 nm of the average particle size as confirmed by size distribution analysis using PSA. The dispersion, colloidal properties and stability of nanoparticle confirmed by zeta potential. The value of zeta potential was highly negative which proved that the silver nanoparticles are stable and used in further experiment. The FTIR analysis also showed the active peaks, which proves active bonds present in the sample and can be used for decolorization of methylene blue dye by interacting with it. The nanoparticles successfully adsorbed methylene blue dye at 3 mg/L concentration with 6 hrs of incubation time.

Keywords: silver nanoparticles, dye removal, particle size distribution, zeta potential, fourier transform infrared spectroscopy

1. Introduction

In present time, dyes are extensively used as coloring agent in textile, paper, paint, leather, cosmetic, pharmaceuticals, food and other industries to make products more attractive. Most of the industries use synthetic dyes containing azo compound as main component for their purposes [1,2]. Every year approximately 1.6 million tons of the variety of dyes has been produced and 10 to 15 % of this has been regularly discharged as effluent waste in open environment [3]. Besides their advantages of making product attractive, the dyes are also responsible for serious health and environmental issues. When they are used as food additives can result in allergies, hyper activity and may even lead to cancer due to their mutagenic and teratogenic properties [4]. They are also environmentally hazardous, as the effluent wastewater containing unused and partially used dyes from above industries has been disposed of in open environment without proper treatment. These harmful dyes from effluent can percolate to ground water via soil leading to environmental pollution [5].

Due to above said implications it is very necessary to prevent the discharge of untreated effluent waste in environment. Several conventional methods are available for dye removal which includes photocatalytic degradation [6], adsorption by activated carbon [7], electrochemical oxidation [8], ozonation [9], coagulation and flocculation treatment [10], nanofiltration membranes [11] and forward osmosis [12]. All these methods are conventional methods and suffer from one or more drawbacks related to inefficiency and providing low surface exchange for the removal of dyes. Further, varieties of adsorbents have been used for adsorption of dye on surface of adsorbent. These adsorbents are palm oil [13], calcium biochar [14], geopolymer paste [15], leaf based adsorbent [16], microcrystalline cellulose [17] etc. They offer a good surface area for degradation of toxic dyes but the efforts should be made for enhancing surface area of pre-existing adsorbents or to develop new adsorbents having better surface area.

For offering better surface area, nanoparticles are more reliable which can efficiently adsorb dye on their surface and degrade them successfully. Now a days nanoparticles are used in various field in healthcare, agriculture, biosensing, environmental monitoring and even in dye removal with great efficiency [18]. In one of the studies zinc oxide nanoparticles has been used for photocatalytic degradation of rhodamine B and indigo carmine [19]. Other nanoparticles have also been used for successful dye removal includes iron oxide [20], stannic oxide [21], iron doped zirconia [22], starch coated magnetic nanoparticles [23], polymer core shell [24], cobalt [25], magnesium aluminate [26], starch coated magnetic nanoparticles [27].

Among the above said nanoparticles, silver nanoparticles are very less exploited. Their inherent properties must be explored in the various analytical and biochemical methods. Therefore, the present research has been focused on synthesis of silver nanoparticles and their further applications in removing methylene blue dye from wastewater.

2. Experimental

2.1. Chemicals and Instrumentation

Silver Nitrate ($AgNO_3$) and trisodium citrate were used for the synthesis of silver nanoparticles (AgNPs) and methylene blue were obtained from Himedia. The synthesized nanoparticles were characterized using UV-Visible spectroscopy (UV-Vis), Particle Size Analyzer (PSA), Zeta Size Distribution, are used from Central Instrumentation Facility, Maharshi Dayanand University, Rohtak, India. Fourier Transform Infrared Spectroscopy was from Department of Biotechnology, University Institute of Engineering & Technology, Maharshi Dayanand University, Rohtak, India. All chemicals used for this study were of analytical grade. Distilled water was used throughout the experiment.

2.2. Synthesis of Silver Nanoparticles

The AgNPs were chemically synthesized and used for dye removal. AgNPs were used for decolorization of methylene blue dye. The synthesized nanoparticles were stored at 4℃ before use and further experimentation.

2.3. Characterization of AgNPs

The AgNPs were first characterized using UV-Vis spectroscopy. The absorbance peak obtained by UV-Vis spectroscopy analysis will provide absorbance of sample under investigation. Further, for confirming nano size of particles present in sample it was subjected to PSA. The PSA will provide size distribution by intensity analysis results to confirm average size of particles present in sample. The size distribution analysis was done at a standard temperature of 25ºC with water as dispersant and a system count rate of 449.5 kcps. The sample was further subjected to Zeta sizer, which will provide information about the conductive nature of the particles at a negative potential. The same standard conditions maintained for Zeta analysis that were used for size distribution analysis. For confirming exact shape and size of particle, which are being synthesized, the sample was subjected to TEM. The sample was also investigated with FTIR to know about different bonds present in the sample.

2.4. Dye removal using the Ag NPs

After successful confirmation of AgNPs synthesis, they were used for kinetic study of methylene blue dye decolorization. The concentration of dye and nanoparticles plays a crucial role in adsorption of process. In first step, absorbance of methylene blue was checked between 400-800 nm. After getting the maximum absorbance peak, a standard graph was plotted and used for determining adsorption capacity of adsorbent. Different dye concentrations form 5mg/L to 2mg/L were used for adsorption of dye on AgNPs. The graphs were plotted between concentration vs time of incubation to check the adsorption capacity of adsorbent. The absorbance of adsorbent containing dyes at different concentrations was analyzed for 10 hours with regular time interval. The schematic representation of the experiment has been depicted in Figure 1.

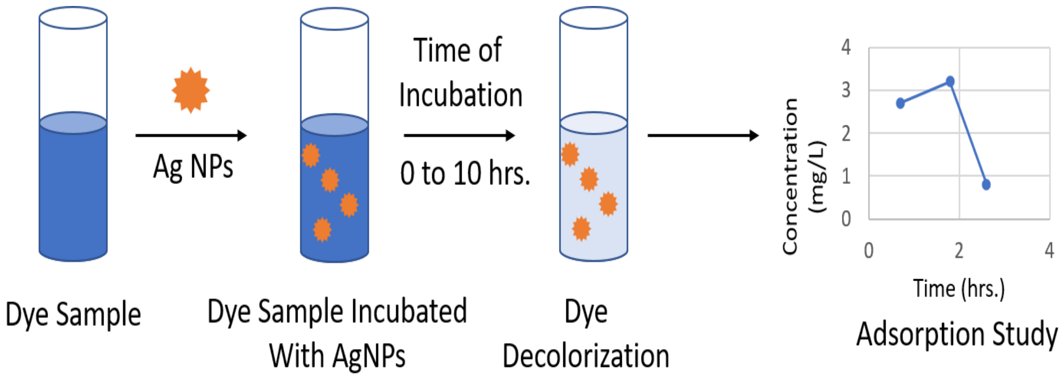

Figure 1: Schematic representation of the experiment

3. Results & Discussion

3.1. Characterization of the stored Ag NPs

The characterization of AgNPs was done with UV-Vis spectroscopy, PSA, zeta potential, TEM and FTIR analysis. The UV-Vis results showed an absorbance peak at 425 nm which confirms the presence of silver in sample as reported in Figure 3. The sample was then subjected to PSA which confirms that average particle sized of AgNPs was 47 nm as shown in Figure 4. A negative value of -19.9 mV was observed with zeta potential results which proved that the stored nanoparticles are highly dispersible, stable for long time and good colloidal nature as shown in Figure 5. TEM results successfully confirmed that the particles are in nano range and spherical in shape as shown in Figure 2. FTIR analysis showed the peaks around 671, 721, 1317, 1648, 1867 and 1919 cm^{-1} which are the signature peaks of AgNPs as shown in Figure 6. All these characterization techniques proved that the synthesized nanoparticles are active and exhibit good characteristics of nanoparticles which can be successfully used to degrade the toxic dyes.

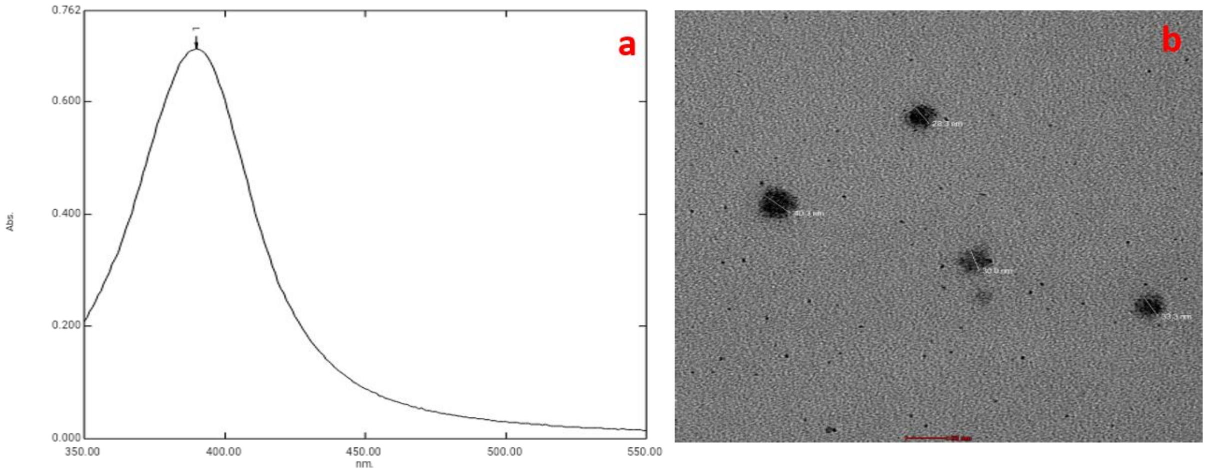

Figure 2: UV-Vis peak of Ag NPs during synthesis (a) and Transmission Electron Microscopic Image of the Ag NPs (b)

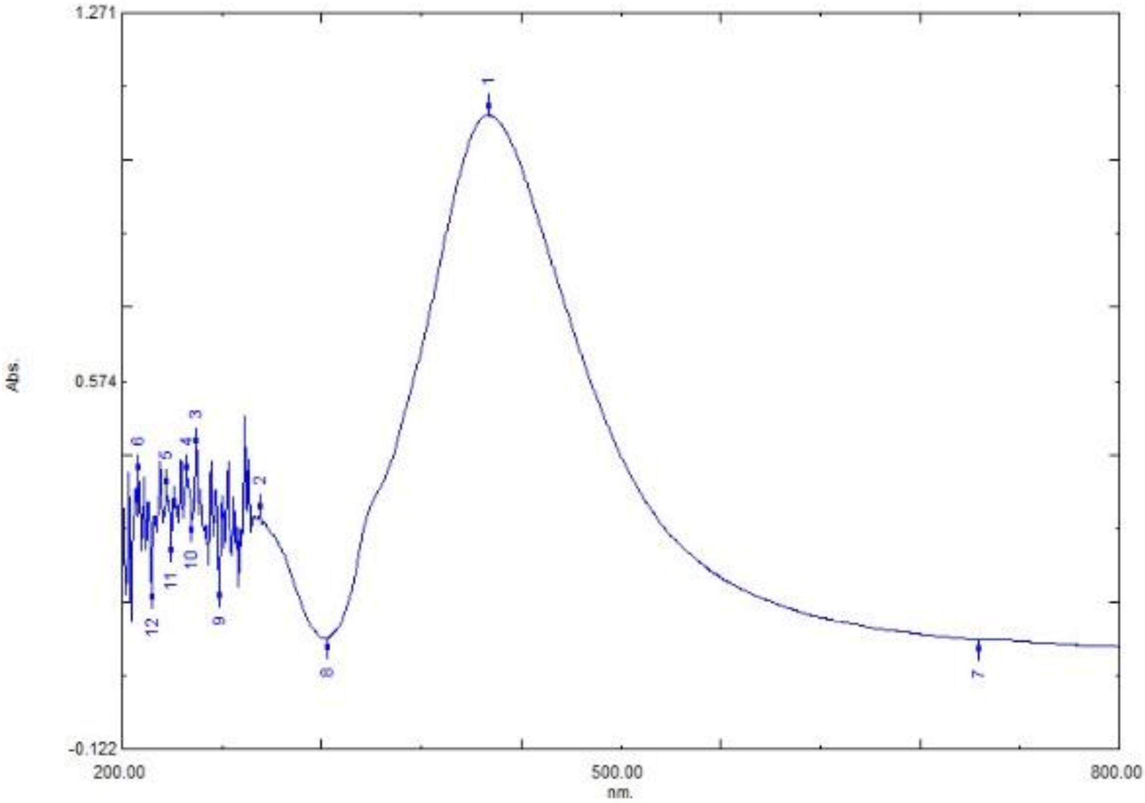

Figure 3: UV-Vis absorbance peak of the Ag NPs after storage at 4ºC

Results

			Size (d.n...	% Intensity:	St Dev (d.n...
Z-Average (d.nm):	47.34	**Peak 1:**	125.1	76.6	99.57
PdI:	0.758	**Peak 2:**	10.10	15.3	4.707
Intercept:	0.780	**Peak 3:**	3507	8.1	1234
Result quality	**Refer to quality report**				

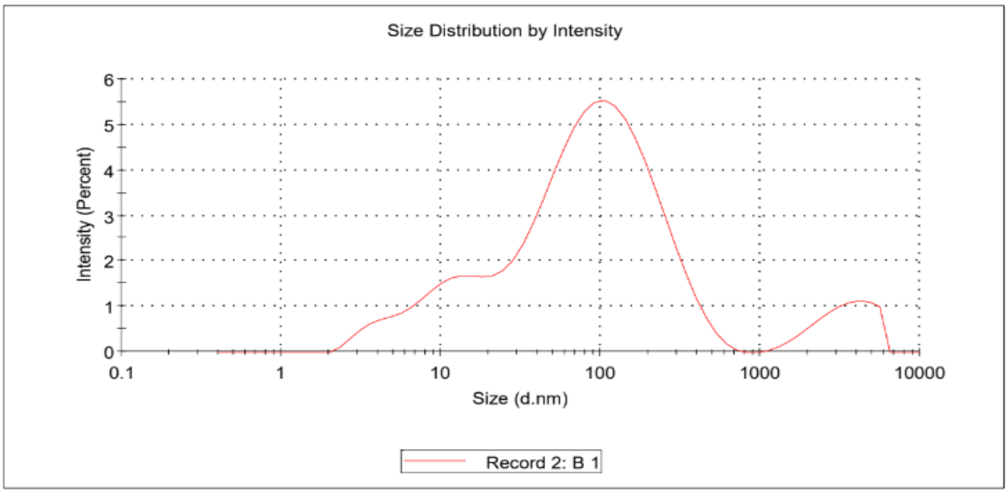

Figure 4: PSA results of the Ag NPs after storage

			Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV):	-19.9	**Peak 1:**	-19.9	100.0	5.46
Zeta Deviation (mV):	5.46	**Peak 2:**	0.00	0.0	0.00
Conductivity (mS/cm):	0.218	**Peak 3:**	0.00	0.0	0.00
Result quality	**Good**				

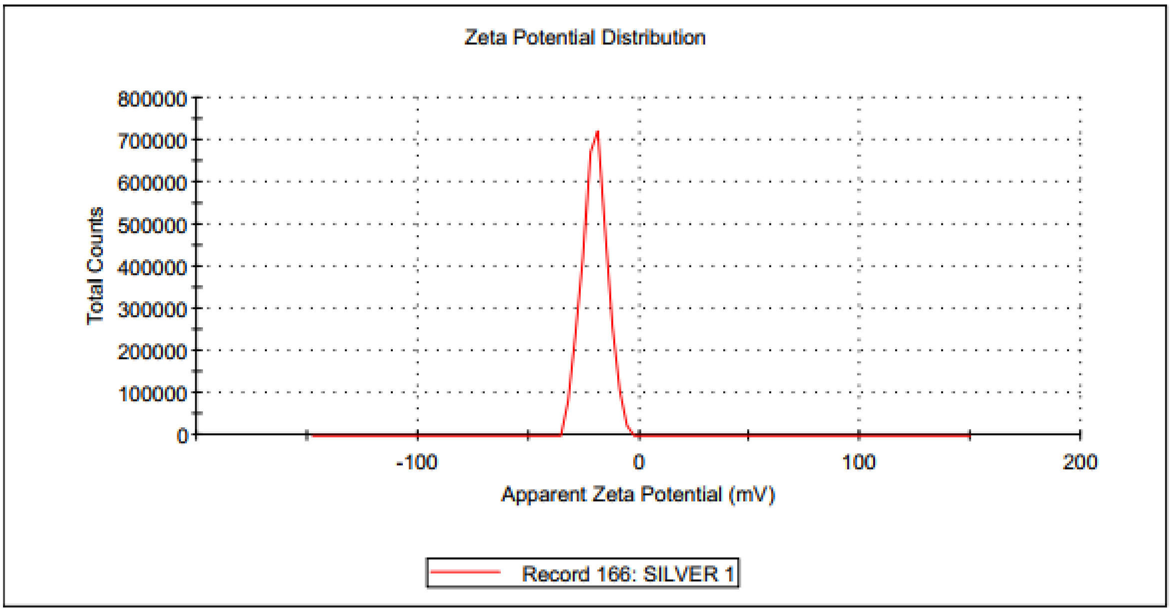

Figure 5: Zeta potential of Ag NPs after storage at 4°C

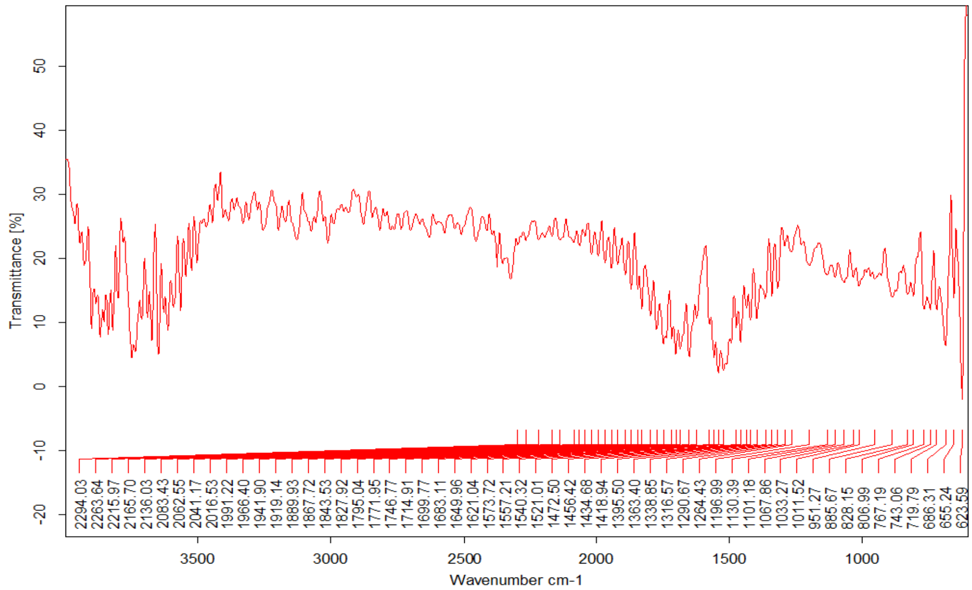

Figure 6: FTIR analysis of stored sample of Ag NPs

3.2. Decolorization of methylene blue dye using Ag NPs

Methylene blue dye showed maximum absorbance at 620 nm in aqueous solution and using this absorbance standard graph was plotted for different concentrations of methylene blue dye is shown in Figure 7. Different concentrations of the dyes have been prepared from the stock solution, which is prepared by adding 5 mg of dye in 1L of distilled water. The four concentrations 5 mg/L, 4 mg/L, 3mg/L and 2 mg/L of methylene blue were used for adsorption study by the pre synthesized AgNPs. Amount of adsorbent used was 5 mg, which was added to the different concentrations of the methylene blue mentioned above for adsorption study. When incubated with the adsorbent, the maximum adsorption was observed with 3 mg/L concentration in which the dye was fully decolorized in 6 hrs. as shown in Figure 8. At other three concentrations, the adsorbent required more incubation time for the removal of dye with less efficiency. This may be due to saturation between nanoparticle surface and dye, which hinders adsorption capacity of nanoparticles.

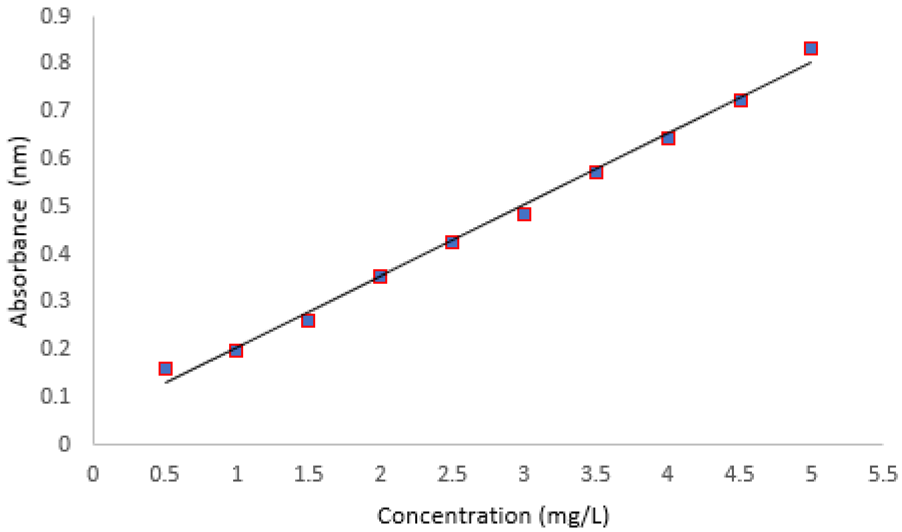

Figure 7: Standard graph of methylene blue absorbance at different concentrations

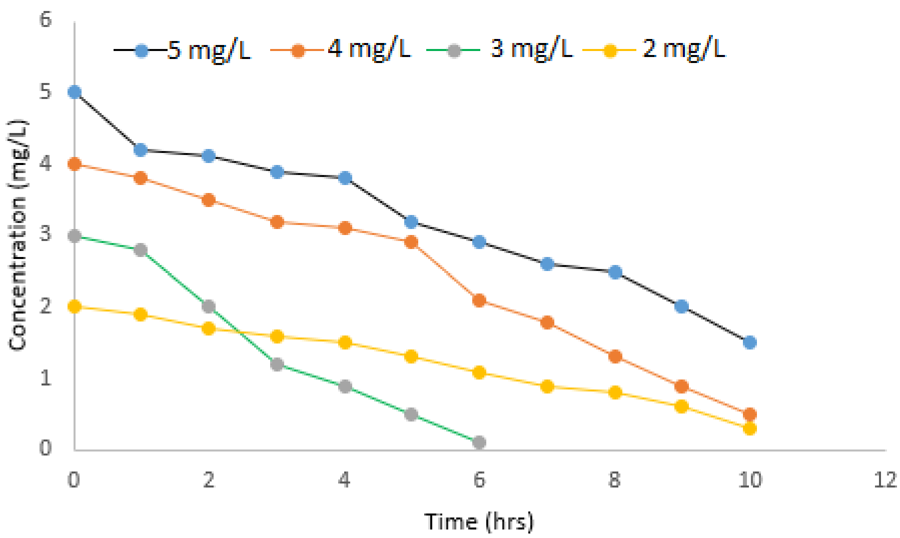

Figure 8: Adsorption of dye at different concentrations of methylene blue

Conclusion

The present method successfully reported use of silver nanoparticles for dye removal in the aqueous medium through adsorption. The pre-synthesized silver nanoparticles were active as confirmed by various characterization techniques such as UV-Vis, PSA, zeta potential and FTIR. The Ag NPs offered large surface area for degradation of methylene blue dye on their surface. It was observed that nanoparticles with average size 46 nm readily dispersed in dye containing solution due to their highly negative zeta potential. As a result of this the nanoparticles remain highly stable in the aqueous medium. When the dye with concentration 3 mg/L was exposed to nanoparticles for 0 to 10 hrs. the color of methylene blue completely disappeared in 6 hrs. So, this method can be used for dye removal from the textile and other industries effluent.

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Conflict of Interest

The authors declare “no conflict of interest” in publication of this research article.

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