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Isotherm and kinetic studies on nano-sorption of malachite green onto *Aspergillus flavus* mediated synthesis of silver nano particles

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ABSTRACT

Enhancement of silver nano particle production by microbial method has been carried out using response surface methodology (RSM). The parameters viz., temperature, concentration of *A. flavus*, silver nitrate concentration and pH were optimized to enhance the production of silver nano particle. The change of color during nanoparticle formations was analyzed using UV–vis spectrophotometer. X-ray Diffraction (XRD) Scanning Electron Microscope analysis (SEM) and Fourier Transform Infrared spectroscopy (FTIR) analysis were carried out to study the morphology and presence of functional groups in the synthesized silver nanoparticles respectively. Decolourization ability of the synthesized nano particles was tested for malachite green (MG) dye. The parameters viz. quantity of AgNP addition, pH and temperature were optimized using RSM. At the optimized conditions, experiments were carried out at various initial dye concentrations and contact time. The results shows that the synthesized AgNP decolorizes MG dye efficiently. From the equilibrium and kinetic studies, it was also found that the D-R isotherm and Intra particle diffusion model fits the data well, respectively.

1. Introduction

As an emerging technology nanotechnology attracts researchers from many fields like physics chemistry, electrical engineering, material sciences and life sciences especically in biomedical application and biotechnology (Catherine, 2012; Kruis et al., 1998; Pankhurst et al., 2003). The advantage of nanotechnology is that it utilizes the special properties that materials possess in nanoscale dimensions (1–1000 nm). Nanomaterials, due to their sheer size show unique and considerable changed physical, chemical and biological properties compared to their macroscale counterparts (Li et al., 2001). Due to their chemical reduction properties, high surface area and surface reactivity of nanoparticles, they can be used as an alternative and highly effective solution for the environmental cleanup. The developments of new chemical and physical methods, the concern for environmental contaminations are also high as the chemical methods concerned in the synthesis of nanoparticles make a large amount of hazardous by products. Hence, a clean, nontoxic and ecofriendly method of nanoparticle synthesis is a possible solution so as to remove the negative effects faced. Microbe mediated synthesis holds the key as an alternative method. (Mukherjee et al., 2001). A novel idea for the production of nanomaterials is provided by traditional synthetic methods and biological systems (Bansal et al., 2011). In microbe mediated Nanoparticles, the target ions from their environment is taken up by the microorganisms. Using the enzymes generated by various cellular activities, it turns the metal ions into the elemental metal. The well-known attribute of many microorganisms including fungi is that production of nanoparticles from inoganic materials is possible by both intracellular as well as extracellular. As an excellent secretors of protein fungi produce higher yield of nanoparticles. Mostly nanoparticles are synthesized extracellularly by fungi. Due to their enormous secretary components, they help in the reduction and capping of nanoparticles resulting stabilization. The proteins secreted by fungi are responsible for hydrolyzing metal ions quickly and through nonhazardous processes. During biosynthesis of nanoparticles, reaction involves reduction/oxidation of substrates, giving rise to colloidal structures. Microbial enzymes possess reducing properties or antioxidants are usually responsible for reduction of metal compounds into their respective nanoparticles. Moreover use of nanoparticles produced from microbe in various experimental processes reduces the risk of use microorganism directly in those works, where such use is associated with various health related risks.

Dyes have major applications in wide scale industries. Various dyes are manufactured to meet the requirement of each type

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of industries. Industries where dyes used in a variety of products include paper and pulp, textiles, adhesives, art supplies, beverages, ceramics, construction, cosmetics, food, glass, paints, polymer, soap, wax biomedicine etc. Thus with this whole range of use its impact on the environment also is wide. They cause various hazards and health related effects (Suchatrita, 2014). Dyes are so problematic because the families of chemical compounds that make good dyes are also toxic to humans. One such dye is Malachite Green. Malachite green is traditionally used as dye. Millions of kilograms of MG and related triarylmethane dyes are produced annually for this purpose (Thomas and Mayer, 2002). Animals metabolize malachite green in its leuco form. The metabolite is retained in catfish muscle longer than its parent molecule (Veterinary Residues Committee, 2001-3). There is also possibility that MG caused carcinogenic symptoms (Culp et al., 2002). However its use is inevitable due to wide range of applications. Thus it is necessary that the dye must be treated in order to reduce its harmful effects.

There are few works available on the removal of dyes by silver nano particles (Junejo et al., 2014; Vanaja et al., 2014; Evangelin et al., 2014; Pal et al., 2013) synthesized by biological methods. So for no work has been carried out for the enhancement of silver nano particle production. Hence, the objectives of this study are, to enhance the production of silver nano particle by microbial methods using RSM and to check the efficiency of synthesized silver nano particles for the removal of malachite green dye.

2. Materials and methods

2.1. Materials

In this study analytical grade chemicals were used. Silver nitrate and malachite green were purchased from Himedia labs and Merck Ltd., India, respectively. Silver nitrate solution was prepared using deionized water and it was stored in dark coloured bottles to avoid photosensitive reaction of silver nitrate when exposed to light. The dark coloured bottles were stored in refrigerator. *Aspergillus flavus* was utilized for the synthesis of silver nanoparticles. The microorganism was purchased from MTCC, Chandigarh, maintained and grown in 100 mL of potato dextrose broth at 25 °C.

2.2. Experimental design by RSM

RSM is a statistical tool employed to optimize the process variables through second order equation. Box Behnken design (BBD) was employed to study the effects of parameters on the response during synthesis of silver nano particle and decolourization process. A statistical tool, Design expert (7.1.5) was employed for the analysis of the data obtained. Analysis of variance (ANOVA) was used to analyze the data. All the experiments were performed in triplicate and the average value was reported.

2.3. BBD for maximum production of silver nano particles

To maximize the production of silver nanoparticles, response surface methodology was used to find the optimum conditions of the parameters viz., temperature, concentration of *A. flavus*, silver nitrate concentration and pH. The ranges of the process variables studied were given in Table 1.

2.4. Procedure for microbial synthesis of silver nanoparticles

Aspergillus flavus was grown in 100 mL of potato dextrose broth at 25 °C, for 48 h. After the incubation, mycelia biomass was separated by filtration, washed with sterile distilled water to remove traces of media components. Then it was resuspended in 100 mL distilled water and incubated at 25 °C. After, 24 h, the culture was mixed well and the suspension was filtered through Whatmann filter paper no. 42. This filtrate was used for the synthesis of silver nanoparticles.

Table 1
Experimental range and levels of independent process variables for Ag-NP production.

Independent variable		Coded Levels		
	Code	−1	0	1
Temperature (°C)	A	30	60	90
pH	B	6	8	10
Concentration of $AgNO_3$ (mg/ml)	C	0.6	2	3.4
Concentration of *A. flavus* (mg/ml)	D	1	2	3

Table 2
Experimental range and levels of independent process variables for decolorization of MG using synthesized Ag-NP.

Independent variable		Coded Levels		
	Code	−1	0	1
pH	A	5	7	9
Temperature (°C)	B	30	45	60
NP Dosage (g)	C	0.1	0.5	0.9

2.5. Characterization of silver nanoparticles

2.5.1. UV–vis spectroscopy analysis

The confirmation of formation of AgNP is done by checking the transformation of color from pale white to dark brown color. The formed AgNP were scanned in the absorption spectra range of 200–800 nm to confirm them.

2.5.2. Fourier transform infrared spectroscopy

FTIR studies were carried for both fresh and MG loaded silver nanoparticles. The study gives the respective functional groups present in the silver nanoparticles present before and after the adsorption process.

2.5.3. X-ray diffraction

XRD is a powerful tool to analyze the crystalline nature of the materials. It show changes in the crystallinity of the adsorbent due to the adsorption reaction.

2.5.4. Scanning electron microscopy

The morphology of the synthesized AgNP were analyzed by SEM before and after decolorization process.

2.6. Batch adsorption experiment for malachite green

Batch adsorption experiments were carried out for the removal of MG dye based on BBD design using synthesized AgNP particle. Table 2 presents the range and levels of the process variables. During experimentation, initial dye concentration was fixed at 100 ppm. Batch sorption experiments were carried out in 250 mL conical flask. The reaction mixtures were agitated in incubated shaker. The samples were taken out and centrifuged at 10,000 rpm for 15 min. Supernatant was analyzed for dye concentration using spectrophotometer. The analyses were repeated thrice and the average value is repeated. The amount of dye adsorbed per unit mass of adsorbent (q_e, mg/g):

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

The amount of adsorbed dye per unit mass of adsorbent at time t (q_t, mg/g):

$$q_t = \frac{(C_o - C_t)V}{m} \quad (2)$$