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A comparative study of synthetic and natural coagulants for silver nanoparticles removal from wastewater

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ABSTRACT

Use of silver nanoparticles is increasing in different packaging material as disinfectant to protect food and pharmaceutical products. Its use has raised the contamination risk of fresh water and human exposure can cause serious problems. The coagulation/flocculation process can be an attractive option for silver nanoparticles removal at small-scale treatment just after its use. Four coagulants, aluminum sulfate, ferric chloride, *Ocimum basilicum*, and *Hibiscus esculentus* (synthetic and natural) were applied. For coagulation/flocculation activity, a series of jar test experiments were conducted to treat silver nanoparticles at concentration of 1 mg L^{-1} from wastewater. *H. esculentus* efficiently removed silver nanoparticles (98.7%) from aqueous solution at a dose of 150 mg L^{-1}, whereas at same coagulant dose, ferric chloride, *O. basilicum*, and aluminum sulfate successfully removed silver nanoparticles at 96, 69, and 50%, respectively. No broad change in pH was observed and it remained between 6.5 and 7.5 during all the experiments at room temperature.

Keywords: Silver nanoparticles; Flocculation; Jar test; *Hibiscus esculentus*; *Ocimum basilicum*

1. Introduction

Silver nanoparticles (AgNPs) are the most widely used nanoparticles (NPs) because of their antimicrobial action with a wide range of applications in consumer goods such as biomedical devices, packaging of food, air and water filters, electronic appliances, cosmetics, clothing/textiles, and cleaning agent as well [1–4]. The potential application of silver nanoparticles in catalysis, sensing, and surface-enhanced Raman scattering (SERS) is the reason behind its abundant use in consumer's products [5]. The huge incorporation of silver nanoparticles in consumer products has led to the increasing concern about their release into the environment, especially in wastewater [6]. Silver

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nanoparticles may cause toxicity to human like weight loss, hypoactivity, altered neurotransmitter level, altered liver enzyme, and immunological effects [7]. Removal of AgNPs from wastewater by coagulation can be a cheap and effective process. Natural or synthetic coagulants are allowed to form aggregates to destabilize the opposite charged particles which then settle down [8–10]. The removal efficiency of AgNPs through coagulation depends on the types of coagulants used, pH of aqueous solution, the natural organic matter, and presence of suspended solids. The use of coagulants also depends upon the nature of the chemicals present in water that needs to be treated [11]. Most common coagulants are aluminum and iron salts [12] such as ferric chloride ($FeCl_3$). There are many problems associated with the use of synthetic coagulants [13] such as cost as well as the environmental contamination [11–14] and community health concerns such as Alzheimer disease [8,11] and production of large amount of sludge [3,13]. Silver nanoparticles were successfully removed at neutral pH using polyaluminum chloride and poly ferric sulfate. In a study, manganese ferric hydroxide was investigated and successful mercury removal was found as compared with polyaluminum chloride [14].

Besides synthetic coagulants, natural coagulants have also been used for treating wastewater [8,13], and these are preferred because of being safe for aquatic system, reduces the treatment cost if locally available [10,11], and biodegradable [15]. The common natural coagulants include *Opuntia ficus indica* (Cactus), peel of Dolichus Lablab (*Hyacinth beans*) [12], seed coat of *H. beans*, *Moringa oleifera* seeds, leaves of *Solanum inacunum*, leaves of *Calotropis procera*, leaves of *Azadirachta indica*, *oppuntia* spp., *Arachis hypogaea* (peanut) seeds, and *Ocimum sanctum* [16]. The *Oppuntia* species of cactus was used as a coagulant for turbidity removal 98% at pH 10. Besides these, common beans *Phaseolus vulgaris*, black locust *Robinia pseudoacacia*, carob *Ceratonia siliqua*, and indigo bush *Amorpha fruticosa* can also be used as natural coagulant where they are locally available [15]. The efficiency of different coagulants at the optimum dosage of 20–200 mg L^{-1} were observed to remove turbidity up to 84% using seed coat of *H. beans*, 22% by peel of *H. beans*, 26.39% by leaves of *C. procera*, 20% by leaves of *S. inacunum*, 20% by leaves of *A. indica*, and 85.2% for *M. oleifera*. The results indicated that among different natural coagulants, the seeds of *M. oleifera* were most efficient for turbidity removal [8]. *M. oleifera* seed biomass was also studied to perform biosorption of metals followed as decreasing order of removal of Cu, Cd, Ni, and Mn [17]. In another study by Sharma, Cd removal 85% by shelled *M. oleifera* seed powder from laboratory scale aqueous solution [18]. *Abelmoschus esculentus* seeds were used for biosorption to remove acid blue dye 113 in aqueous solution was found 169 mg g^{-1} at 25˚C [19].

The main purpose of this study was to explore the removal of AgNPs from wastewater by comparing locally available natural coagulants, *Hibiscus esculentus*, *O. basilicum*, and synthetic coagulants aluminum sulfate and ferric chloride.

2. Materials and methods

2.1. Jar test apparatus

The four paddles, stainless steel "jar apparatus" SSjartest_1_Sargos, were used in the present study with variable speed (manufactured by Sargos Compressors Company, Hattar Industrial Estate, District Haripur, KPK, Pakistan). It was used for the mixing and facilitating the contact of coagulants with AgNPs. The solution was first allowed for rapid mixing for 3–4 min at a stirring speed of 200 rpm and then shifted to slow stirring speed of 100 rpm for 30 min. Then sample was allowed for 3 h settling and decant was separated for the analysis of AgNPs by atomic absorption spectroscopy.

2.2. Synthetic coagulants

The commonly used coagulants such as ferric chloride ($FeCl_3{\cdot}6H_2O$) and aluminum sulfate $Al_2(SO_4)_3{\cdot}16H_2O$ [18] were selected for the experiments because these are easily available and low cost. Initially 50, 100, 150, and 200 mg L^{-1} solutions of aluminum sulfate and ferric chloride were prepared separately by dissolving 50, 100, 150, and 200 mg of coagulants in 1,000 ml of distilled water. Aluminum concentration from aluminum sulfate was 4.2, 8.56, 12.85, and 17.13 mg L^{-1} and iron from ferric chloride 10.35, 20.70, 31.05, and 41.40 mg L^{-1} was present in the coagulant dose. Synthetic wastewater sample containing AgNPs at concentration of 1 mg L^{-1} was treated against different doses of synthetic coagulants using jar test apparatus. The solution was first allowed to mix for 3–4 min at stirring speed of 200 rpm and then shifted to slow stirring speed of 100 rpm for 30 min. The sample was then allowed for 3-h settling and decant was separated for atomic absorption spectroscopy.

2.3. Natural coagulants

Both synthetic coagulants and natural coagulants were tested to see the silver removal from contaminated water [20]. The natural coagulants selected for this study were *H. esculentus* and *O. basilicum*. The dried seeds of *H. esculentus* and *O. basilicum* obtained from a local Pansaar (herbal/homeopathic) store were ground and sieved to obtain the size of 354 μm. Different dilutions such as 50, 100, 150, and 200 mg L^{-1} of natural coagulants were prepared.

Jar test apparatus was used for the mixing of AgNPs solution against natural coagulant of 5, 10, 15, and 20 mg L^{-1}. The same methodology was used for mixing as used for synthetic coagulant. The sample was then allowed for 3-h settling and decant was separated for atomic absorption spectroscopy.

3. Results and discussion

3.1. Removal of AgNPs with synthetic coagulants

The AgNPs-contaminated wastewater with 1 mg L^{-1} concentration was treated against different coagulant doses 50, 100, 150, and 200 mg L^{-1} of aluminum sulfate and the removal efficiency of AgNPs was 22, 50, 68, and 75%, respectively. It was observed with increasing coagulant doses, the percent removal of AgNPs was increased. The maximum removal was observed with coagulant dose of 200 mg L^{-1} aluminum sulfate. The result of coagulation activity is illustrated in Fig. 1. Higher than 200 mg L^{-1} of alum doses might increase TDS value therefore more addition was avoided [21].

Silver nanoparticles in water present in the form of Ag^{-} (negative charge), when aluminum salt dissolved in water then aluminum sulfate breaks down into Al^{3+}, $Al(H_2O_2)_2^{3+}$, $Al(OH)^{2+}$, $Al(OH)_2^{+}$ which are effective to adsorb onto the surface of negative charge colloidal [22]. In this case, AgNPs removal takes place due to the charge neutralization between aluminum sulfate and AgNPs.

Different concentrations 50, 100, 150, and 200 mg L^{-1} of ferric chloride [$FeCl_3{\cdot}6H_2O$] were used as a coagulant for the removal of 1 mg L^{-1} solution of AgNPs. The removal (%) of AgNPs increases with the increase in coagulant doses. The removal efficiency of AgNPs was 92.5, 96.2, 97.2, and 97.8% using ferric chloride dose of 50, 100, 150, and 200 mg L^{-1}, respectively. The result indicates that maximum coagulation of 97.8% occur by the use of 200 mg L^{-1} of ferric chloride in wastewater (Fig. 2).

3.2. Comparison of aluminum sulfate and ferric chloride in silver nanoparticles removal

The comparison was drawn between the ferric chloride [$FeCl_3{\cdot}6H_2O$] and aluminum sulfate [$(Al_2(SO_4)_3{\cdot}16H_2O$] as coagulants for AgNPs removal from aqueous solution. Ferric chloride and aluminum sulfate both show maximum removal of AgNPs 97.8 and 75%, respectively, at dose 200 mg L^{-1} (Fig. 3) at pH 6–7.5.

3.3. Removal of silver nanoparticles with natural coagulants

3.3.1. Hibiscus esculentus

Different concentrations 50, 100, 150, and 200 mg L^{-1} of *H. esculentus* were used as a coagulant for treating wastewater containing 1 mg L^{-1} AgNPs. The result shows, with the increase in coagulant doses, the percent removal of AgNPs also increases with removal efficiency was 58, 87, 98.7, and 99% with *H. esculentus* at coagulant

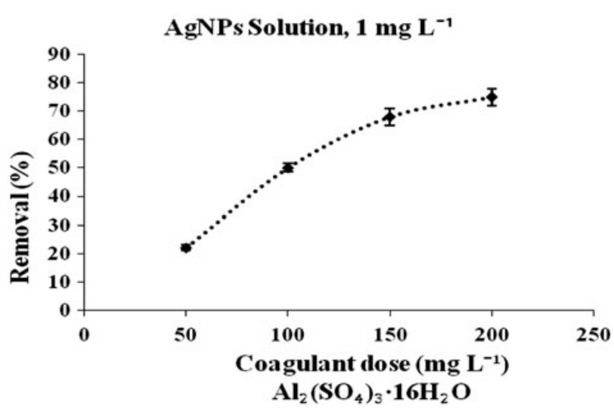

Fig. 1. Removal (%) of AgNPs with different alum doses, error bars indicated the standard deviation of triplicate samples.

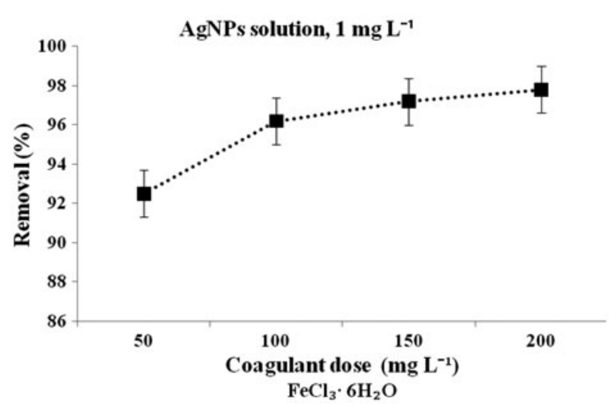

Fig. 2. Removal (%) of AgNPs with different $FeCl_3{\cdot}6H_2O$ doses, error bars indicated the standard deviation of triplicate samples.

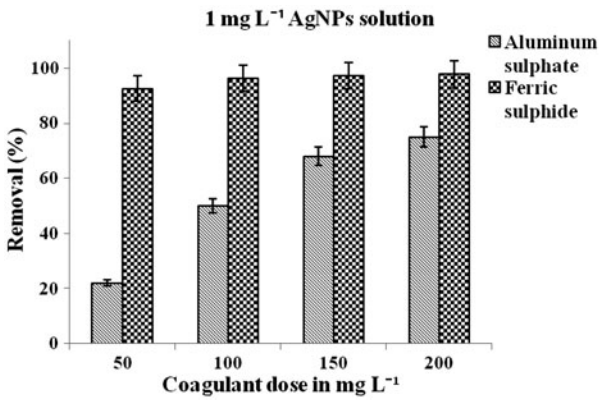

Fig. 3. Comparison of removal (%) of AgNP with aluminum sulfate and ferric chloride for 1 mg L^{-1} AgNPs. Error bar indicates the standard deviation of triplicate samples.

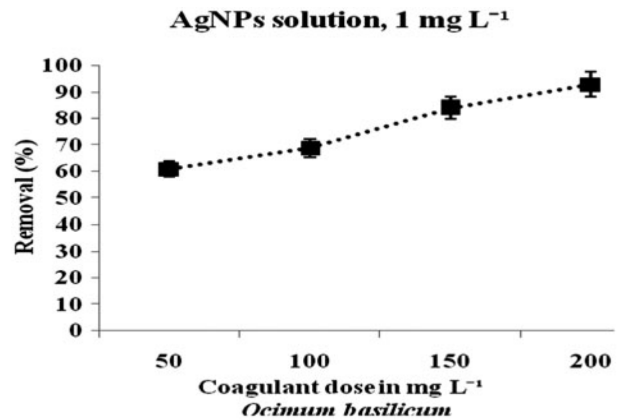

Fig. 5. Removal (%) of AgNPs with different *O. basilicum* doses, error bars indicated the standard deviation of triplicate samples.

dose of 50, 100, 150, and 200 mg L^{-1}, respectively. The results revealed that maximum coagulation of 99% happens by the use of 200 mg L^{-1}*H. esculentus* against 1 mg L^{-1} AgNPs (Fig. 4).

3.3.2. Ocimum basilicum

Ocimum basilicum was used against 1 mg L^{-1} solution of AgNPs as a natural coagulant in concentration ranges from 50 to 200 mg L^{-1}. The increased dose of *O. basilicum* increased the maximum coagulation of AgNPs. The removal efficiency of AgNPs by *O. basilicum* was 61, 69, 84, and 93% for 50, 100, 150, and 200 mg L^{-1}, respectively. The maximum coagulation of 93% was observed by the use of 200 mg L^{-1} against 1 mg L^{-1} AgNPs (Fig. 5).

3.3.3. Comparison of H. esculentus *and* O. basilicum *in silver nanoparticles removal*

The comparison between *H. esculentus and O. basilicum* was drawn for the removal of AgNPs from aqueous solution. *H. esculentus and O. basilicum* both have shown maximum adsorption at the dose of 200 mg L^{-1} i.e. 99 and 93%, respectively. The comparison of both coagulants is given below in Fig. 6.

3.4. Comparison of synthetic and natural coagulant for silver nanoparticles removal

In Fig. 7, ferric chloride and *H. esculentus* are more efficient coagulant for silver nanoparticles removal. Ferric chloride was found more efficient at 50 mg L^{-1} dose as compared with natural and synthetic coagu-

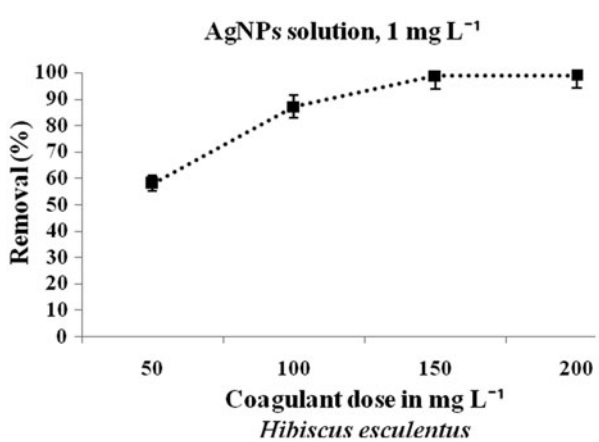

Fig. 4. Removal (%) of AgNPs with different *H. esculentus* doses, error bars indicated the standard deviation of triplicate samples.

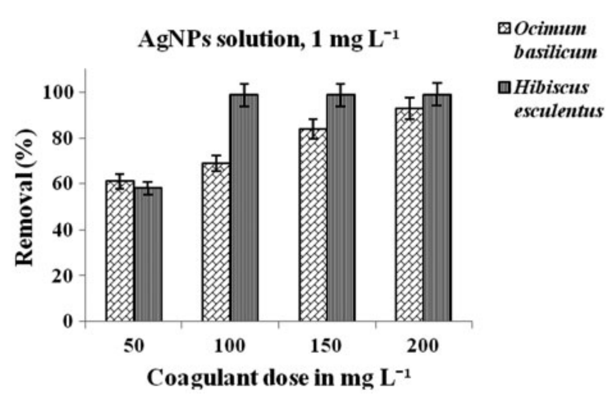

Fig. 6. Comparison of removal (%) of AgNP with *H. esculentus* and *O. basilicum* for 1 mg L^{-1} AgNPs. Error bar indicates the standard deviation of triplicate samples.

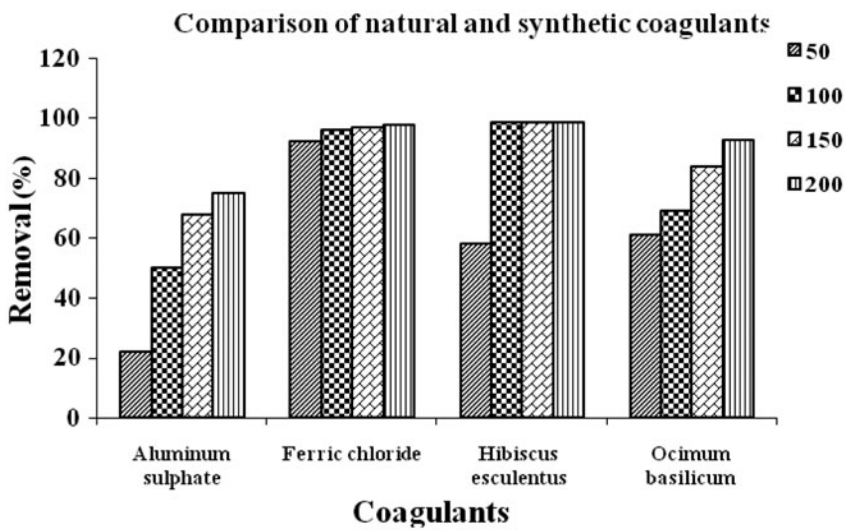

Fig. 7. Comparison of synthetic and natural coagulant for silver nanoparticles removal.

lants. In this study, *H. esculentus* was found effective, environmentally friendly, and natural flocculants for AgNPs removal.

It was also considered that the synthetic flocculent like aluminum sulfate whose residues in treated water may cause Alzheimer [23]. The use of *H. esculentus* was scarcely reported for AgNPs removal with 99% removal efficiency.

The composition of *H. esculentus*, genotype in Pakistan, is Mn 4.6, Fe 34.4, Cu 1.5, Zn 7.9, Na 43, Mg 519, Ca 1639, and P 488 mg/100 g where as ash 10.35%, fiber 21.5%, fat 1.85%, protein 18.88%, and CHO 47% are reported [24]. In another study, electrocoagulation techniques were used to treat silver nanoparticles from synthetic effluent. Four different chemicals were used, and the results included 98% removal with sodium citrate used as reducing and stabilizing agent, 99.9% removal with sodium borohybride as reducing agent, 99.8% with D-glucose and sodium pyrophosphate as stabilizing agent, and 99.9% removal with sodium pyrophosphate as stabilizing and sodium borohybride as reducing agent [25]. Activated sludge biological flocs were also used successfully to remove silver nanoparticles [26].

4. Conclusions

The coagulation study includes the use of synthetic as well as natural coagulants. The use of synthetic coagulant indicated that ferric chloride [$FeCl_3 \cdot 6H_2O$] showed greater removal (%), i.e. 97.8% than aluminum sulfate. Aluminum sulfate [($Al_2(SO_4)_3 \cdot 16H_2O$] removal was 75% at 200 mg L^{-1}. As chloride ion in ferric chloride is more electronegative than sulfate ion in aluminum sulfate, and silver being highly electropositive shows greater affinity toward highly electronegative chloride ion than sulfate ions. Thus, ferric chloride showed more coagulation with silver. However, the results of natural coagulants such as *H. esculentus* and *O. basilicum* revealed that both the coagulants showed effective removal of AgNPs from aqueous solution, but *H. esculentus* proved to be more significant than *O. basilicum* with maximum AgNPs percent removal of 99% for 200 mg L^{-1}.

It can be concluded that an increased coagulant dose can increase the removal (%) of AgNPs by coagulation. The maximum coagulation or AgNPs removal took place at 200 mg L^{-1} concentration of coagulant but it should not be more than 200 because increase in TDS also contributes in treated sample.

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