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Co-precipitation with calcium carbonate – A fast and nontoxic method for removal of nanopollutants from water?

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Abstract

Presence of nanosized contaminants such as engineered Gold (Au), Silver (Ag) nanoparticles and Graphene oxide (GO) in many commercial products are creating environmental concerns owing to their high toxicity. Removal of such nanomaterials (NMs) from water using current technologies is not very efficient owing to small size and shapes of such pollutants. Here we explore a fast method for the extraction of NMs from aqueous solutions based on *insitu* co-precipitation of calcium carbonate particles. Removal efficiency was estimated using batch adsorption studies. Co-precipitation method entraps and removes the nanomaterials in a fast and efficient manner to purify water. Microscopic observation and spectrophotometric analyses indicated the extraction and incorporation of NMs into the calcium carbonate precipitate. Complete removal (99 %) of metal nanoparticles and graphene oxide was observed within 10 min during the co-precipitation and settling of the solids. This method is efficient to remove nanopollutants from water at low concentration (ppm) levels. Co-precipitation, a simple and scalable purification method using nontoxic material can be scaled up to treat contaminated industrial effluents.

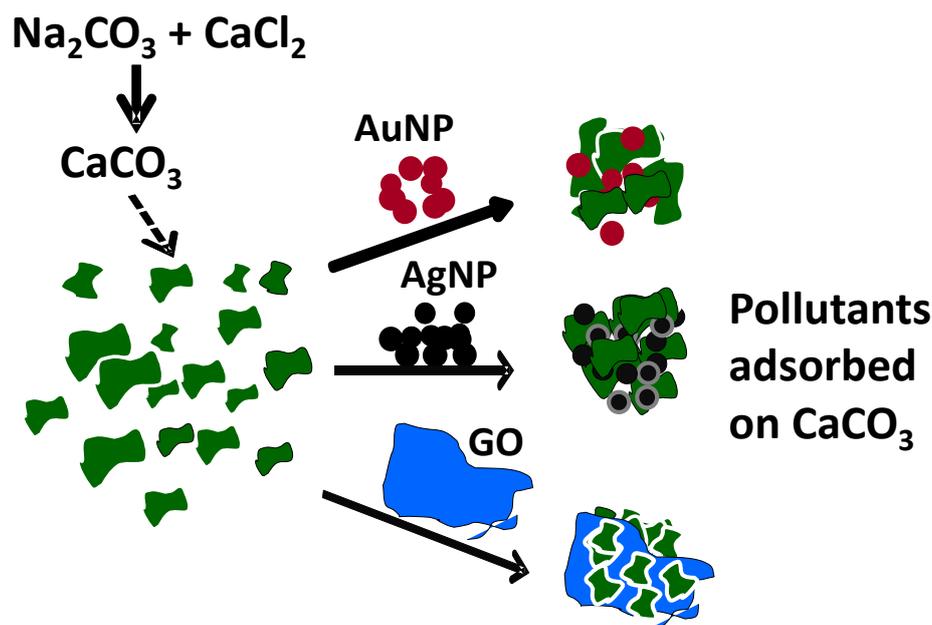
Keywords: Co-precipitation, calcium carbonates, nanomaterials, nanopollutants

Introduction

Currently nanomaterial research is an area of intense scientific interest owing to a wide variety of potential applications in biomedical, optical and electronic industries. The production and usage of nanomaterials are rapidly increasing, especially in consumer products such as clothing, children's toys, house-hold products, and personal care products.¹⁻³ The engineered nanoparticles are an emerging class of contaminants with an expected wide spread distribution in the water system. Unregulated usage and disposal of nanomaterials incorporated products increase human and environmental exposure to nanoparticles, which leads to increased toxicity and adverse health issues in living systems. Many nanomaterials such as Ag, TiO₂, ZnO and Au nanoparticles are already found in wastewater and industry effluents.^{4,5} The entry of nanoparticles into human body occurs through multiple path ways such as direct skin contact, inhalation and by dietary intake of contaminated products.⁶⁻⁸ Recent *in vitro* and *in vivo* studies have demonstrated the toxicity of silver and gold nanoparticles in mammalian cells and living organisms.⁸ Silver nanoparticles are reported to cause significant DNA damage and mitochondrial impairment in mammalian cells.⁷ Current concentration of nanoparticles in natural surface waters are in the nanogram/L to microgram/L range (i.e. parts per trillion to parts per billion), but the concentrations may increase with greater usage of nanoparticle incorporated products. Latest results indicate that these particles can persist in natural water bodies, and are not fully removed during water purification steps, thereby posing a potential public health concern.⁵

Recently, a few methods were reported for the removal of nanocontaminants from water including coagulation and aggregation.⁹⁻¹¹ Water treatment technologies include filtration, precipitation, oxidation, coagulation and anion exchange, all of them are known to remove pollutants. However, none of the above water treatment methods successfully demonstrated

removal of nanoparticles due to small size and large variation in composition. *In situ* precipitation of calcium carbonate (CaCO_3) is an alternative method for the removal of nanomaterials owing to the tendency of nanoparticles to adsorb on emerging CaCO_3 particles in solution. Co-precipitation has been successfully used for the removal of dyes¹² and toxic metal ions¹³ from water. Low solubility, nontoxic nature and easy separation/filtration of the CaCO_3 precipitate makes this process an efficient and easy to implement under rural areas. Co-precipitation of CaCO_3 to remove Ag NMs, Au NMs and graphene oxide nanomaterials from water is explored in this study (Scheme 1). In addition, effect of various factors such as ionic strength and rate of precipitation towards the removal of nanomaterials via precipitation of CaCO_3 is also investigated.



Scheme 1. Extraction of nanopollutants using co-precipitation. The objects are not in scale.

Materials and methods

Materials

Sodium carbonate (Na_2CO_3), Calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), Sodium borohydride (NaBH_4), Silver nitrate (AgNO_3), Hydrogen auric chloride ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), Polyvinyl pyrrolidone (PVP)

and Graphene oxide (GO) were purchased from Sigma-Aldrich. Stock solutions of Au-PVP NMs and Ag-PVP NMs were prepared using a reported procedure.¹⁴⁻¹⁶ Ultrapure water was used in all experiments.

Synthesis of gold and silver nanoparticles

Polymer capped silver and gold nanoparticles in aqueous solution were prepared via reduction of corresponding salts with NaBH₄. PVP (0.1 g) dissolved in water (3 mL) and added to HAuCl₄·3H₂O or AgNO₃ (100 mmol) solution in water. The mixture was diluted with water (50 ml) and stirred at room temperature. NaBH₄ (0.01 g) dissolved in water (3 ml) was added drop wise to the stirring solution. The colourless solution became dark red in case of Au, grey in the case of Ag, indicating the formation of nanoparticles. The solution was stirred for a day and the nanoparticles (NPs) were purified by repeated centrifugation and washing with water. After removing the traces of starting materials through washings, the solid residue was dispersed in water and lyophilized to get pure NPs. Appropriate amount was used for making the stock solution of NMs.

Experimental procedure: Co-precipitation

Na₂CO₃ and CaCl₂ solutions (0.5 mL, 0.05 M) were added to the aqueous solution of the nanomaterial (1 mL, 5 - 80 ppm). The solution was stirred (150 rpm) at room temperature (25 °C) and CaCO₃ precipitate formed instantaneously after mixing the precursor solutions. It is noted that the stirring speed and rate of addition did not influence removal efficiency of NMs from water. The solid precipitate was allowed to settle and supernatant liquid was analyzed for the presence of NMs using elemental analysis and Uv-Vis spectroscopy. An optimal settling time of ca 10 minutes was selected. In order to decrease the settling time, the solution was centrifuged (5000 rpm) and the supernatant liquid was collected for analysis. Settling time and speed of centrifugation did not change the extraction efficiency of NMs. Control experiments

were performed to investigate the separation of NMs during centrifugation and observed that high speed around 25000 rpm was required for aggregation, followed by separation of NMs.

Quantitative measurement of nanomaterials using Uv-Vis spectroscopy

PVP capped Au NMs and Ag NMs showed absorption maxima at 520 nm and 397 nm, respectively, in water which were similar to the reported values in the literature¹⁷ (Figure 2). Similarly, The GO showed absorption maximum at 220 nm, consistent with the value reported in the literature.¹⁸ Stock solutions of all three nanomaterials were prepared and calibration curves were created using concentrations and intensity at the absorbance maximum. Absorbance of solution after extractions were measured and concentrations were established using the calibration curve.

Characterisation methods

Morphologies of CaCO₃ precipitates were characterised using JEOL JSM-6701F Field Emission Scanning Electron Microscopy (FESEM). All samples were coated with platinum metal before SEM analysis to make the surface conductive. Energy dispersive X-ray spectroscopy (EDS) was done in conjunction with SEM to investigate the chemical composition of the precipitate. NMs were characterised using a JEOL 2010-F Field Emission Transmission Electron Microscope (FETEM). Size and zeta potential measurements of synthesized NMs were done using Malvern Zetasizer Nano-ZS90, UK. The quantitative measurements of NMs were carried out using a Shimadzu-1601 PC UV-Vis spectrophotometer.

Results and discussion

Characterization of NMs

The synthesized metal NMs are in the size range of 15 - 20 nm (Figure 1). NMs were further characterized using zetasizer to understand the hydrodynamic size and aggregation properties in solution (Table 1). As expected, the hydrodynamic diameter (30 – 35 nm) of NMs is higher than the TEM measurements (15 – 20 nm) owing to the hydration and all NMs showed negative zeta potential. The data from DLS analysis describing size and zeta-potential are given in supporting information.

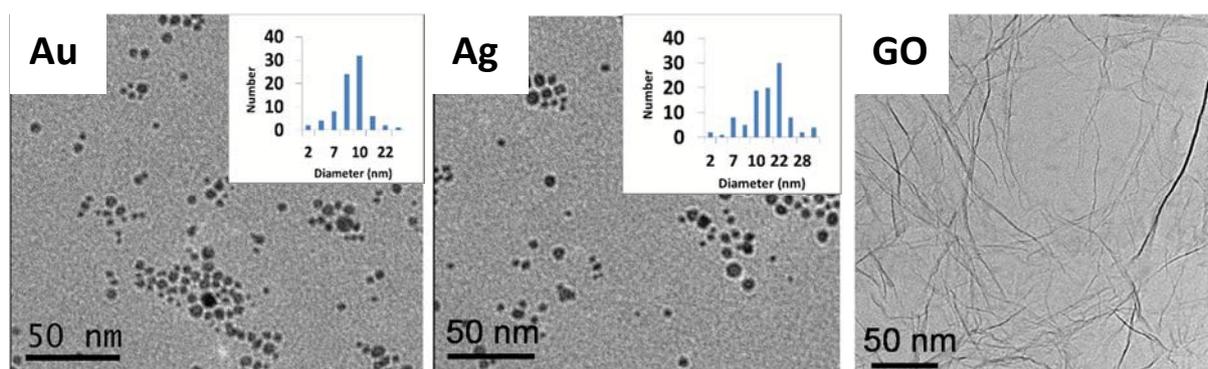


Figure 1. TEM images of Ag NMs (a), Au NMs (b) and GO (c) inset are the size distribution plots.

Table 1. Size and surface charge analysis of NMs using DLS.

Nanoparticle	Size (nm)	Zeta potential (mv)
Au – PVP	30.9± 0.6	- 14.1± 0.8
Ag – PVP	35.2± 0.2	- 22.1± 1.6
GO	300.2± 0.1	- 28.2± 0.9

The Au and Ag NMs showed Uv-Vis adsorption due to surface plasmon resonance and the spectra of all NMs were recorded in water (Figure 2). PVP capped nanoparticles showed characteristic absorption maxima, intensities of which were used to measure the concentration of nanoparticles left in the solution after extraction. Similarly, The GO showed absorption maximum at 220 nm, consistent with the value reported in the literature.¹⁸

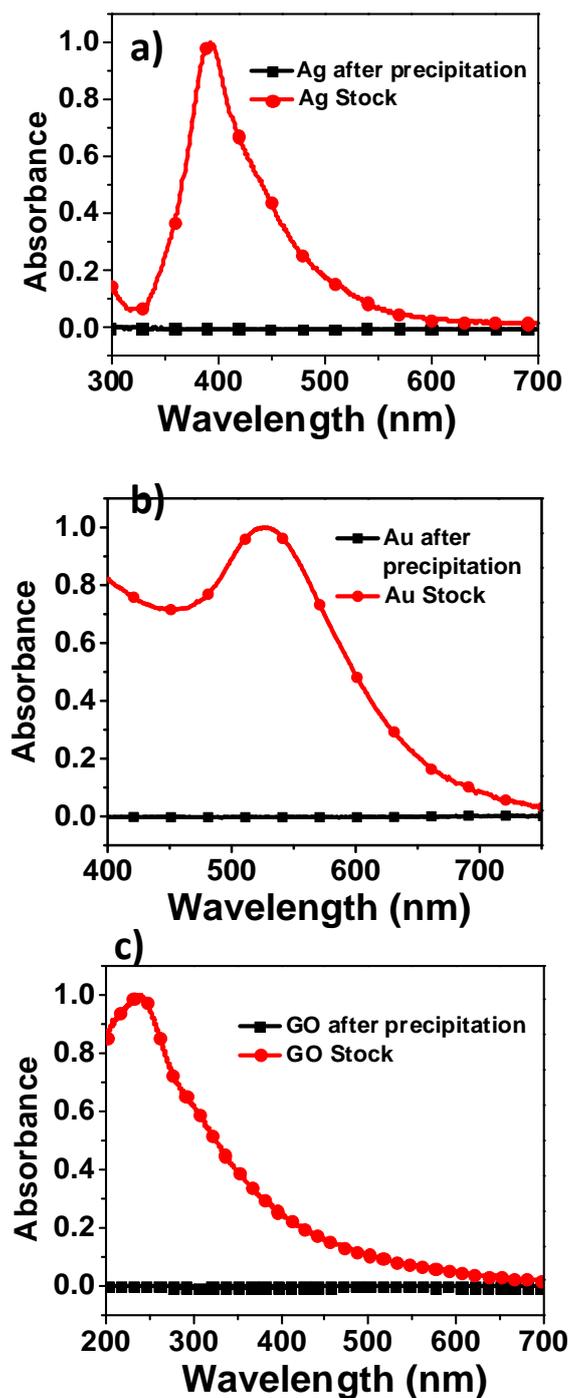


Figure 2. UV-Vis spectra of Ag NMs (a), Au NMs (b) and GO (c) before and after the precipitation.

Removal of nanoparticles: Equal volumes of Na_2CO_3 and CaCl_2 solutions (0.5 mL, 0.05 M) were added to the aqueous solution of the nanomaterial. Upon mixing, a white precipitate was formed instantly and the supernatant liquid was separated after settling the precipitate.

Solutions were analysed before and after precipitation using UV-Vis spectroscopy to estimate the concentration of NMs in solution. The relationship between the concentration of seeding solutions and the amount of NMs extracted is investigated using several extraction studies. After carrying out the precipitation experiments at different concentrations (0.025, 0.05, 0.1, 0.2, 0.5 and 1 M) of Na_2CO_3 and CaCl_2 solution, the optimum concentration of Na_2CO_3 and CaCl_2 solutions required for efficient removal of NMs was determined as 0.05 M for 1 mL of NMs solution (5 ppm). As expected, the extraction efficiency increased with increase in concentration of Na_2CO_3 and CaCl_2 solutions. However, an optimum concentration was selected to achieve maximum efficiency with minimum amount of CaCO_3 precipitate. Figure 3 illustrates the gradual increase in the removal of NMs as the concentration of Na_2CO_3 and CaCl_2 was increased. The extraction efficiency of different NMs using co-precipitation method was evaluated from the data obtained (Figure 3). It is estimated that 1 g of CaCO_3 can extract 24.32 mg of Au, 13.27 mg of Ag and 156.27 mg of GO, respectively.

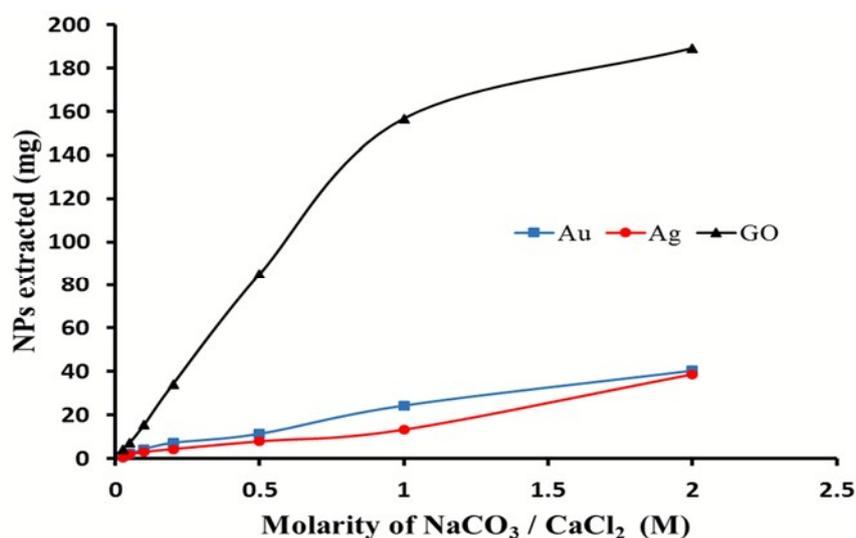


Figure 3. Extraction of NMs by varying the concentration of Na_2CO_3 and CaCl_2 . Equal volumes (0.5 mL) of the solutions were used for the precipitation under ambient conditions.

Concentrations of NM solutions were varied from 1 ppm to 100 ppm to check the dosage effect on the removal efficiency. Equal volumes of Na_2CO_3 and CaCl_2 (0.5 mL, 0.05 M) solutions were added to different concentrations of NMs solutions and allowed to settle for 10 min. All extraction experiments were done at room temperature and neutral pH. The residual concentration of nanomaterials in the supernatant solution was analysed after removing the precipitate. Figure 4 illustrates the removal efficiency of the precipitation method towards different NMs. During the experiment, the solution become colourless and the precipitated CaCO_3 become coloured based on nanoparticles used, which indicated the incorporation of NMs into CaCO_3 precipitate. The percentage of extracted NMs was calculated by using the following equation,

$$\text{Percentage removal} = ((C_i - C_f) / C_i) 100 \quad (1)$$

where C_i and C_f (mg / L) are concentrations of NMs at initial and final conditions. Effect of NMs dosage in the extraction process is investigated by varying NMs concentration and keeping the concentration of seeding solutions constant. The initial concentrations of NM solutions used were 1, 2, 5, 10, 20, 40 and 70 mg / L and the experiments were carried out for 20 min. Figure 4 shows the extraction efficiency of precipitation method towards different nanomaterials investigated at various concentrations.

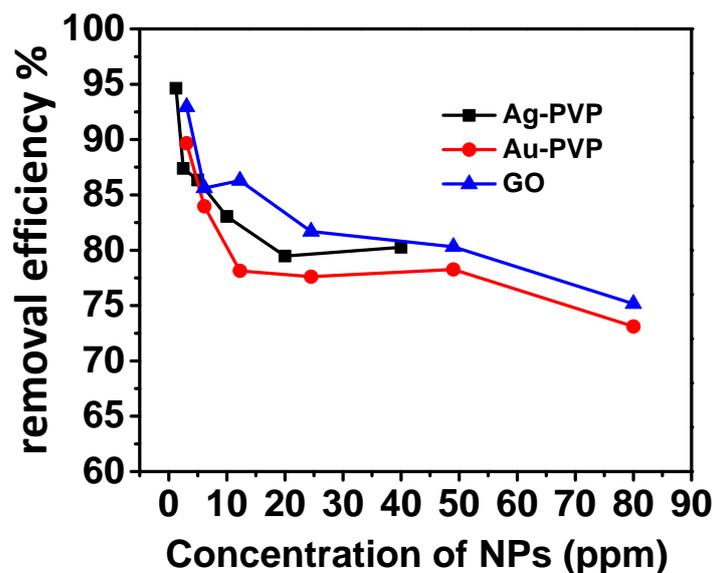


Figure 4. Removal efficiency of NMs at various concentrations under ambient conditions.

It is clear from Figure 4 that an optimum concentration of Na_2CO_3 and CaCl_2 solutions (0.05 M, 0.5 mL) is sufficient to extract NMs (5 ppm, 1 mL) from water. By increasing the concentration of Na_2CO_3 and CaCl_2 solutions beyond the optimum concentration, no significant improvement in the extraction efficiency was observed (Figure 3). Also, the enhancement in the extraction efficiency decreases with increase in concentration of nanomaterials, indicating a proportional relationship between the NMs concentration and the concentrations of Na_2CO_3 and CaCl_2 solutions exist in the precipitation process.

Removal of NMs by co-precipitation might be affected by the presence of other interfering ions in the medium. Effect of ionic strength on the removal of NMs was studied by adding different concentrations of NaCl (0.1, 0.2, 0.5, 0.8, 1, 1.5, and 2 M) in to the solution. Figure 5 demonstrates the changes in extraction efficiencies of NMs with different concentrations of NaCl solutions. It is noted that presence of NaCl did not influence adversely to the removal capacity of the method.

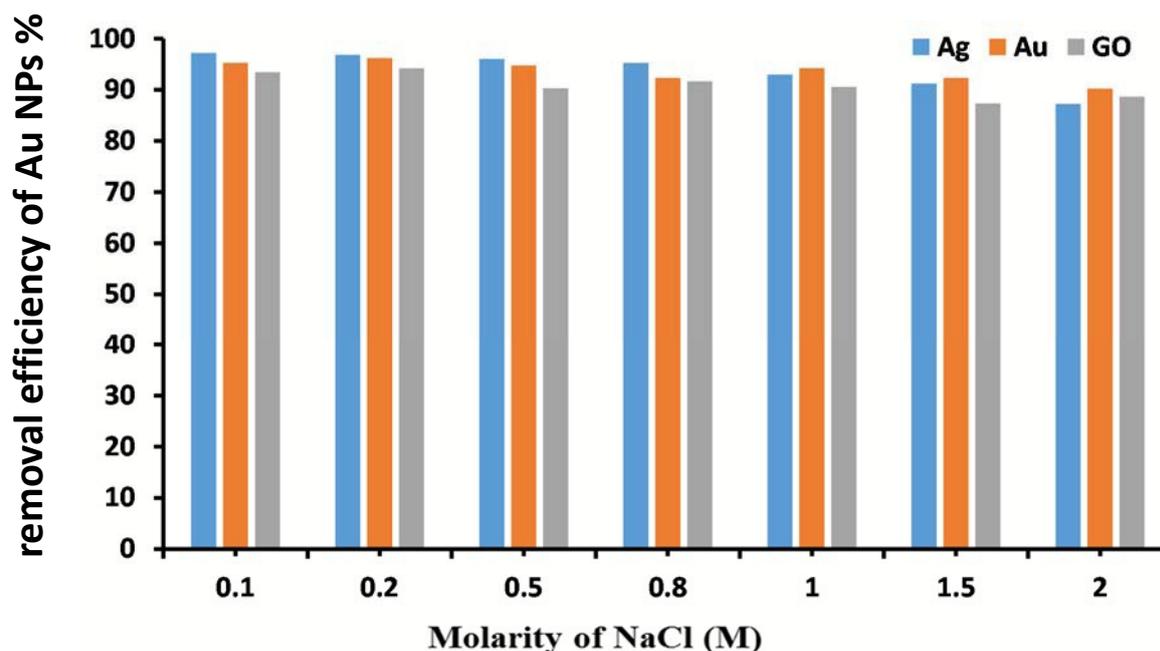


Figure 5. Percentage removal of Ag NPs, Au NPs and GO from water in presence of different concentrations of NaCl in solution under ambient conditions

Also the rate of addition of Na_2CO_3 and CaCl_2 solutions and precipitation of CaCO_3 precipitation method towards removal of different NMs was investigated. In order to check the rate of precipitation on extraction efficiency, Na_2CO_3 and CaCl_2 solutions were added using two different rates of addition - spontaneous mixing *Vs* slow addition within 5 minutes. After precipitation, the suspended supernatant liquid was analysed for the amount of NMs remaining in solution. Figure 6 shows the extraction of Au NMs with two different rates (0 & 5 min) of coprecipitation. There were no significant differences observed in extraction efficiencies with different rates of addition. Similar observations were found in case of Ag NPs and GO. This result suggests that the extraction of NMs by coprecipitation was affected by the amount of precursor solutions (Na_2CO_3 & CaCl_2) added but not by the rate of addition.

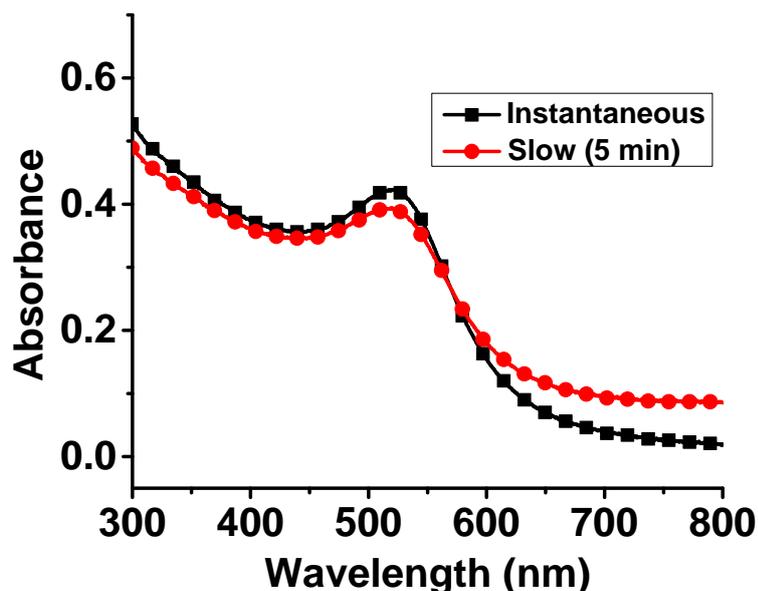


Figure 6. Extraction of Au NMs at two different rates of coprecipitation.

Characterisation of precipitate after adsorption

Mixing of equal volume (0.5 mL) and equal molarity (0.05 M) of CaCl_2 and Na_2CO_3 solutions resulted in the formation and settling of CaCO_3 precipitate (Figure 7). A controlled experiment was carried out by adding separate Na_2CO_3 or CaCl_2 solutions separately to nanoparticle solutions and analysed the concentration of NMs before and after addition. As expected, there was no precipitation or changes in the concentration of NM solutions in both cases. This indicates that neither Na_2CO_3 nor CaCl_2 solutions could interact or entrap nanomaterials from water. The CaCO_3 formed by the addition of both solutions did not settle immediately and took about 10 min to settle from solution. The solution was centrifuged to separate the precipitate, which turns into pink in the case of Au, grey for Ag and black for GO (Figure 7). The remaining solutions become almost colourless indicating the removal of nanomaterials.

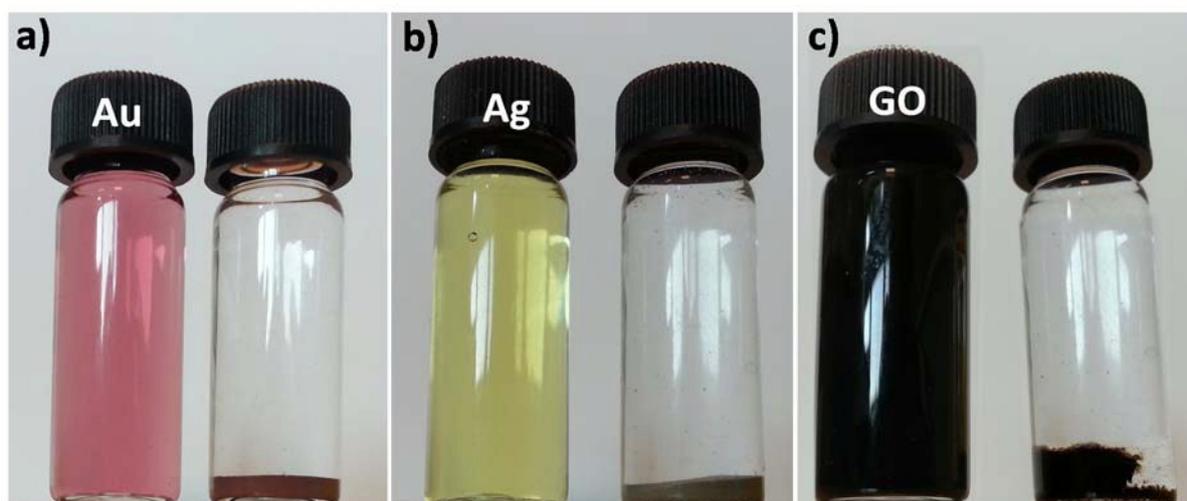


Figure 7. Image illustrating the precipitation of Au NMs (a), Ag NMs (b) and GO (c) by adding Na_2CO_3 or CaCl_2 solutions.

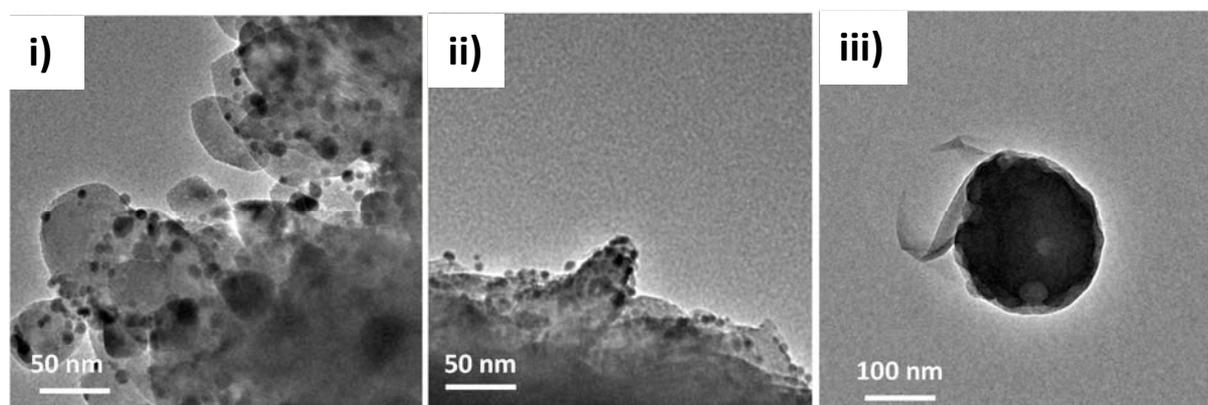


Figure 8. TEM images of Ag NMs (i), Au NMs (ii) and GO (iii) adsorbed on CaCO_3 precipitate.

The surface morphology of the CaCO_3 precipitate was examined using SEM and TEM after entrapping the NMs. FESEM micrographs (supporting information, Figure S4) shows the presence of NMs on the surface of the precipitate. EDS analysis of the precipitate (Supporting information, Figure S1) gave peaks corresponding to the metals (Ag and Au) which further confirms the presence of NMs on the surface. TEM analysis of the samples showed the presence of nanomaterials on the surface of CaCO_3 precipitate. TEM micrographs (Figure 8) showed the surface of the precipitate decorated with NMs and the entrapment of the precipitate by GO sheets. These observations support fast and efficient removal of nanomaterials from water.

Conclusions:

A simple and efficient method for the removal of dissolved Ag NMs, Au NMs and GO from water was developed using a coprecipitation method. The mechanism involves the entrapment of nanomaterials during the *in situ* formation of CaCO₃ precipitate. It is calculated that 1 g of CaCO₃ was able to remove 24.32 mg of Au NMs, 13.27 mg of Ag NMs and 156.27 mg of GO from aqueous solution. Presence of interfering ions did not have significant effect on the removal efficiency. Results indicate that such co-precipitation method could also be used for the effective removal of other pollutants. Easy design, low cost and nontoxic additives are novel features of this water treatment method. The method is scalable and modified to fit water treatment plants due to its simple operation procedure.

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References

1. G. Reiss and A. Hutten, *Nat. Mater.*, 2005, **4**, 725-726.
2. T. Pradeep and Anshup, *Thin Solid Films*, 2009, **517**, 6441-6478.
3. M. Ahamed, M. S. AlSalhi and M. K. J. Siddiqui, *Clinica Chimica Acta*, 2010, **411**, 1841-1848.
4. M. Diallo and N. Savage, *J. Nanopart. Res.*, 2005, **7**, 325-330.
5. C.-J. M. Chin, P.-W. Chen and L.-J. Wang, *Chemosphere*, 2006, **63**, 1809-1813.
6. S. Hackenberg, A. Scherzed, M. Kessler, S. Hummel, A. Technau, K. Froelich, C. Ginzkey, C. Koehler, R. Hagen and N. Kleinsasser, *Toxicol. Lett.*, 2011, **201**, 27-33.
7. Y. Teow, P. V. Asharani, M. P. Hande and S. Valiyaveetil, *Chem. Commun.*, 2011, **47**, 7025-7038.
8. J. S. Teodoro, A. M. Simões, F. V. Duarte, A. P. Rolo, R. C. Murdoch, S. M. Hussain and C. M. Palmeira, *Toxicology in Vitro*, 2011, **25**, 664-670.
9. L. Hou, K. Li, Y. Ding, Y. Li, J. Chen, X. Wu and X. Li, *Chemosphere*, 2012, **87**, 248-252.
10. S. S. Khan, A. Mukherjee and N. Chandrasekaran, *Colloids Surf., B*, 2012, **92**, 156-160.
11. Y. Liu, M. Tourbin, S. Lachaize and P. Guiraud, *Ind. Eng. Chem. Res.* 2011, **51**, 1853-1863.
12. T. Saitoh, M. Saitoh, C. Hattori and M. Hiraide, *J. Environ. Chem. Eng.*, 2014, **2**, 752-758.
13. J. Du, C. Jing, J. Duan, Y. Zhang and S. Hu, *J. Environ. Sci.*, 2014, **26**, 240-247.
14. H. Wang, X. Qiao, J. Chen, X. Wang and S. Ding, *Mater. Chem. Phys.*, 2005, **94**, 449-453.
15. D. L. Van Hying and C. F. Zukoski, *Langmuir*, 1998, **14**, 7034-7046.

16. J. Polte, T. T. Ahner, F. Delissen, S. Sokolov, F. Emmerling, A. F. Thünemann and R. Kraehnert, *J. Am. Chem. Soc.*, 2010, **132**, 1296-1301.
17. Z. Nie, A. Petukhova and E. Kumacheva, *Nat. Nano.*, 2010, **5**, 15-25.
18. K. Vijayaraghavan and S. P. K. Nalini, *Biotechnol. J.*, 2010, **5**, 1098-1110.