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Removal of phenol in aqueous solution by adsorption onto green synthesized coinage nanoparticles beads

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Abstract

The adsorption of phenol from aqueous solution was carried out by using alginate stabilized silver nanoparticles (AgNPs) and gold nanoparticles (AuNPs) beads as adsorbents. The resulting AgNPs and AuNPs were characterized by scanning electron microscope (SEM), UV-visible spectroscopy and fourier transform infrared (FTIR) spectroscopy. Batch adsorption studies have shown that removal is dependent upon process parameters like initial concentration, contact time, pH and adsorbent dosage. The adsorption data obtained from batch studies at optimized conditions have been subjected to Freundlich and Langmuir isotherm studies. The pseudo-first-order and pseudo-second-order kinetic model was also applied to the experimental data. Phenol was effectively removed $90.0 \pm 0.8\%$ from aqueous solution using alginate stabilized AuNPs beads as the adsorption process. Desorption studies were made to elucidate recovery of the adsorbate and adsorbent for the economic competitiveness of the removal system. The alginate stabilized AgNPs and AuNPs beads were found to be good adsorbent for adsorption of phenol from aqueous solution.

Keywords: Silver nanoparticles. Gold nanoparticles. Adsorption. Alginate. Phenol

Introduction

Phenol as phenolic compounds is included in Ministry of Environment and Forest (MOEF), Govt. of India, New Delhi and United State Environmental Protection Agency (USEPA) priority water pollutants list. These compounds are present in effluents of the petroleum refining, coke oven batteries, coal gasification plant, ply board manufacturing industries, etc [1]. Phenolic compounds are very harmful to organisms even at very low concentration due to its toxicity, foul odour and carcinogenic properties [2]. The health effects following repeated exposure to low levels of phenols in water include liver damage, diarrhea, mouth ulcers, dark urine and hemolytic anemia [3]. As per the Bureau of Indian Standards, New Delhi, India, the allowable limit of phenol in drinking water is 1 mg/L while MOEF (Govt. of India) has set a maximum concentration level of 1 mg/L of phenol in the industrial effluents for safe discharge into inland surface water and 5 mg/L for safe discharge into public sewers and marine coastal areas. The world health organization (WHO) recommended 0.001 mg/L as the permissible phenolic concentration in potable water.

It is therefore necessary to reduce or to eliminate such organic pollutants from water and wastewater before discharge or reuse. Various treatment methods are available for removal of organic pollutants which include adsorption, ion exchange, reverse osmosis, chemical oxidation, precipitation, distillation, gas stripping, solvent extraction, complexation and even bioremediation [4]. However, adsorption process is considered to be superior to other techniques for water re-use in terms of initial cost, simplicity of design, use of operation and insensitivity to toxic substances [5]. Adsorption is considered a versatile technology for water and wastewater treatment because very high levels of contaminant removal can often be attained by using an appropriate adsorbent [6]. Adsorption has been used extensively in industrial process for

separation and purification. The removal of coloured and colourless organic species from industrial wastewater is considered as an important application of adsorption processes [7]. Adsorption method is used for removal of many types of organic species by use of different adsorbents [8-24].

Activated carbon (AC) has been widely used as an adsorbent for treatment of wastewater to remove organic and inorganic pollutants [25-26]. Due to high specific surface area, AC frequently exhibit high removal efficiency for most of the dissolved compounds. It has a good capacity for the adsorption of many organic molecules [27]. In spite of this, it suffers from several disadvantages [28] such as its high cost for regeneration, and also the process produces additional effluent resulting in considerable loss of the adsorbent. Over the years, waste materials from agricultural products such as rice straw, coconut husk, peat moss and biomass have been exploited as possible alternatives to use as AC to remove hazardous chemicals from waste water [29]. Biosorption, a popular technique used for pollutants removal from wastewater can be defined as sequestering of organic and inorganic species including metals, dyes and odour causing substances using live or dead biomass or their derivatives. This biomass can be bacteria, fungi, seaweed, sludge from biological wastewater treatment plants or by products from fermentation industries [30]. However, there are some disadvantages of biomass to use as adsorbent for wastewater treatment. The use of dead rather than live biomass eliminates the problem of waste toxicity and nutrients requirements. Biomass adsorption is effective when conditions are not always favourable for the growth and maintenance of the microbial population. To improve the effectiveness and selectivity of the adsorption processes, it is essential to develop more efficient and cost effective adsorbent with higher adsorption capacities.

Metal nanoparticles (NPs) have attracted considerable interest because of their novel properties and their potential application. Accurate controls of size, composition, morphology and stability and the use of environment-friendly procedures are highly desirable for the synthesis of NPs. There have been a number of techniques for NPs synthesis developed over the years using a range of metals [31-39]

In recent year, polymeric adsorbents having wide variations in porosity and surface characteristics have been employed for the adsorption studies of some organic species [40-41]. Alginate is one of the most extensively investigated biopolymer for removal of pollutants from aqueous solution as it is inexpensive, non-toxic and efficient. It is a natural polysaccharide extracted from brown seaweeds. This linear polymer is composed of β -D-mannuronate (M) and α -L-guluronate (G) units linked by β -1,4 and α -1,4 glycosidic bonds M and G units are organized in MM, GG and MG block, the proportion of these block varying with the source of the polymer. Carboxylate group on the polymer give it the ability to undergo a sol-gel transition in the presence of multivalent cations. GG blocks are directly responsible for the gelation process: regions composed of polyguluronate in one alginate macromolecule are; linked to a similar region in another alginate macromolecule around calcium ions in the form of a so-called 'egg-box structure'.

In this paper, green methods to synthesize alginate stabilized silver nanoparticles (AgNPs) and gold nanoparticles (AuNPs) are described. The preparations of AgNPs and AuNPs were carried out by irradiating the solutions under microwave. NPs were characterized by scanning electron microscopy (SEM), UV-visible spectroscopy and fourier transform infrared (FTIR) spectroscopy. The adsorption behavior of phenol by the alginate stabilized AgNPs and AuNPs beads are given in detail in this paper. Adsorption studies were carried out to study the

effects of various experimental parameters such as initial concentration, contact time, pH and adsorbent dose were evaluated. In addition, the equilibrium isotherms, adsorption kinetics and desorption studies of phenol onto the alginate stabilized AgNPs and AuNPs beads were also investigated.

Experimental

Materials and methods

Silver nitrate (AgNO_3) was obtained from Merck, gold chloride (HAuCl_4) was obtained from Aldrich, sodium alginate was obtained from LOBA, calcium chloride (CaCl_2) was obtained from Qualigens and phenol was obtained from Merck were used without further purification. All the solutions were made in triple distilled water. 1×10^{-4} mol/L AgNO_3 , 1×10^{-4} HAuCl_4 mol/L, 0.2 M sodium alginate, 0.1 M CaCl_2 and parts per million solutions of phenol were used.

A Samsung CE2877 domestic microwave oven (850W), Samsung India Electronics Ltd., New Delhi, India was employed for irradiating solutions. The morphology of the alginate stabilized AgNPs and AuNPs beads were characterized by Scanning Electron Microscope (SEM) at the National Centre for Experimental Mineralogy and Petrology, Allahabad. Varian Carry 50 UV-Vis spectrophotometer was used for spectral studies. FTIR spectra were recorded on IR Affinity-1, Shimadzu.

Nano adsorbent preparation

The AgNPs and AuNPs were prepared using a microwave irradiation method. To AgNPs and AuNPs, the following procedure was adopted: Firstly, the reaction solution were prepared by dissolving in triple distilled water 0.2 mol/L sodium alginate and 1.0×10^{-4} mol/L silver nitrate (AgNO_3) in a 50-ml conical flask to obtain a homogeneous reaction mixture. Then the flask was placed on the turntable of the microwave oven. The mixture was irradiated at a power of 300

watt for the duration of 4 min and the reaction was carried discontinuously to prevent an increase of pressure. After irradiation, the dilute colloidal solution with pale yellow colour was cooled to room temperature for characterization. Then the AgNPs beads were prepared by addition of above prepared AgNPs from a syringe (20-ml) into the 0.1 M calcium chloride (40 ml) solution drops wise until the syringe is empty. The colour of the resulted beads was deep yellow. Presence of divalent Ca^{2+} ions causes gelation to form spherical beads having the diameter of ~ 2 mm. Beads were filtered and washed with triple distilled water several times until the washing was Cl^- free. Finally, these beads were stored in triple distilled water for further use. In a similar approach, AuNPs beads were prepared using gold chloride (HAuCl_4) in place of AgNO_3 . The colour of the beads in this case was blue-violet. Figure 1 show the alginate stabilized AgNPs and AuNPs beads.

Adsorption experiments

The efficiency of the phenol removal from aqueous solutions using alginate stabilized AgNPs and AuNPs beads were experimentally studied by recording adsorption isotherms. Batch adsorption studies were carried out using the following experimental procedure:

A standard solution of phenol containing 5 to 40 mg/L was used for batch studies. Batch experiments were conducted using 250-ml conical flask to which 100 ml of phenol containing water and adsorbent were added. These flasks were agitated at room temperature and shaken at a constant speed. After the equilibration period, the adsorbent beads were separated by centrifugation and pollutants in the centrifugate were analyzed UV-visible spectrophotometrically at wavelength of maximum absorbances (λ_{max}), i.e., at 290 nm for phenol.

The percentage removal of the phenol was measured at the optimum adsorption conditions employed for phenol to check the selectivity of alginate stabilized AgNPs and AuNPs

beads. Effect of various process parameters on the extent of removal of phenol was studied.

Percentage removal has been calculated using the following equations:

$$\text{Percentage removal} = 100 (C_i - C_e) / C_i$$

Where, C_i and C_e are initial and equilibrium (final) concentration of phenol (mg/L), respectively.

Desorption studies

The adsorbent was dispersed in adsorbent solution as mentioned in the adsorption procedure. The phenol loaded adsorbents were separated from the mixture solution by centrifugation and washed with acid to remove any adsorbed adsorbate. Desorption experiment was performed by transferring the adsorbate loaded adsorbent into acid and stirred for continuously. After regeneration, the adsorbent was again used for the further adsorption of phenol. Adsorption and desorption experiments were repeated for several cycles.

$$\text{Percent desorption} = \frac{\text{amount of adsorbate liberated by acid}}{\text{amount of adsorbate adsorbed on adsorbents}} \times 100 \%$$

Results and discussion

Characterization of AgNPs and AuNPs beads

A primary tool for characterizing the surface morphology and fundamental physical properties of adsorbent is SEM and useful for determining the porosity of the adsorbents. SEM images of alginate stabilized beads of AgNPs and AuNPs are shown in Fig. 2 (a) and Fig. 2 (b). The Figures showed that AgNPs and AuNPs beads have a considerable number of pores where there is a good possibility for adsorbate to be trapped and adsorbed.

The UV-visible spectrum of alginate stabilized beads of AgNPs and AuNPs are shown in Fig. 3 (a) and Fig. 3 (b). The AgNPs and AuNPs synthesized exhibit strong absorption peaks at 420 nm and 520 nm, respectively. The pale yellow colour of the colloidal solution of Ag sample

provides clear evidence for the formation of AgNPs. Similarly, the purple colour of the colloidal solution of Au samples shows the formation of AuNPs.

The Fig. 4 and Fig. 5 show the spectral segments of FTIR spectra of AgNPs, AuNPs beads and phenol loaded AgNPs, AuNPs beads. In the Gaussian peaks appearing at ~ 1400 and $\sim 1530\text{ cm}^{-1}$ for AgNPs beads and at 1450 and 1615 cm^{-1} for AuNPs beads are due to the symmetric and antisymmetric stretching vibrations of --COO^- respectively. The band at 1635 cm^{-1} could be due to the intramolecular hydrogen bridges. The (--COO^-) band of silver calcium alginate was found at $\sim 1385\text{ cm}^{-1}$. The broad band in the range of 3450 cm^{-1} for AgNPs and 3400 cm^{-1} for AuNPs beads are due to presence of --OH groups [42-43].

Figure 5 shows a significant change in the FTIR spectra observed after the adsorption of phenol on AgNPs (a) and AuNPs (b) beads. Peaks appeared in the region of 3620 , 3080 , 1580 cm^{-1} for AgNPs beads and 3600 , 3095 , 1500 cm^{-1} for AuNPs beads indicate the presence of --OH bond, C-H bond, C=C bond, respectively.

Effect of initial concentration

The effect of initial concentrations on the percentage removal of phenol by alginate stabilized AgNPs and AuNPs beads is shown in Fig. 6 with error bars showing the values of standard deviation ($n=5$). The experiments were conducted at $\text{pH } 4.0 \pm 0.8$ at room temperature. The concentration of phenol was varied from 5 to 40 mg/L . The results show that the value of percentage removal of phenol decreases from 72.0 ± 0.8 to $58.0 \pm 0.8\%$ by AgNPs beads and 90.0 ± 0.8 to $75.0 \pm 0.8\%$ by AuNPs beads respectively.

The value of percentage removal decreases as the concentration of adsorbate increases, indicating that less favourable sites became involved in the process with increasing concentration.

The increase in initial concentration also enhances the interaction between adsorbates and the adsorbents [44].

Effect of contact time

The study of contact time on phenol adsorption from aqueous solutions at $C_o = 5$ mg/L for adsorbent dosage 2 g at room temperature was carried out to determine the equilibrium time. The result is shown in Fig. 7 with error bars showing the values of standard deviation ($n=5$). For a contact time period between 5 to 25 hrs, the percentage removal of phenol for alginate stabilized AgNPs and AuNPs beads are 40.0 ± 0.8 to 72.0 ± 0.8 and 50.0 ± 0.8 to $90.0 \pm 0.8\%$ respectively. The removal percentage increases with the increase in contact time and reveals a rapid removal during the first few minutes of contact until to reach a state of equilibrium in 25 hrs at room temperature. Based on these results, a contact time of 25 hrs was assumed to be suitable for subsequent experiments of adsorption isotherm. Percentage removal of phenol by alginate stabilized AuNPs beads seems to be superior than the alginate stabilized AgNPs beads.

Therefore at the initial stage, the rate of removal of adsorbate was higher, due to the availability of more than required number of active sites on the surface of adsorbents which became slower at the later stages of contact time, due to the decreased or lesser number of active sites [45].

Effect of pH

To study the effect of pH on the percentage removal of phenol, experiments were carried out using different initial solution pH values, varying from 2 to 9. The initial concentration of phenol was measured at the beginning of experiment, when the initial solution pH was adjusted to the desired value. The obtained data are presented in Fig. 8 with error bars showing the values of standard deviation ($n=5$). As pH increases, the extent of removal increases, reaches a maximum

value and then decreases. The optimum pH for removal of phenol is fixed at 4.0 ± 0.8 for alginate stabilized AgNPs and AuNPs beads. Removal due to pH change alone may be due to the structural changes being affected in the adsorbate molecules [46].

Effect of adsorbent dosage

Adsorbent dose is an important parameter in the determination of adsorption capacity. The effect of the adsorbent dose was investigated by the addition of various amounts of adsorbent from 0.5 to 3.0 g in 100 mL aqueous solution of phenol (5 mg/L) at room temperature for equilibrium time. The results are shown in Fig. 9. It is evident from the plots that the percentage removal of phenol from the aqueous solution increases with increase in the adsorbent dosage. The removal efficiency for phenol increased from 15.0 ± 0.8 to $72.0 \pm 0.8\%$ and 20.0 ± 0.8 to $90.0 \pm 0.8\%$ with the adsorbent dose varying from 0.5 to 2 g of alginate stabilized AgNPs and AuNPs beads, respectively. It is readily understood that the number of available adsorption sites increases by increasing the adsorbent dose and it therefore results in an increase in the percentage of phenol adsorbed.

Adsorption isotherm

To examine the relationship between adsorbed amount of phenol and equilibrium concentration adsorption isotherm models are widely employed for fitting the data, of which the Freundlich and Langmuir equations are most widely used. The specific adsorbed amount of the adsorbate on adsorbent was calculated from the initial and equilibrium concentration according to the equation.

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e$$

Where, K_F and n are Freundlich constant, a characteristic of the system indicating the adsorption capacity (mg/g), and adsorption intensity respectively. In order that to follow

Freundlich model perfectly, the plot of $\ln Q_e$ vs $\ln C_e$ for the adsorption of phenol onto the adsorbent should give a straight line with a slope of $1/n$ and intercept of $\ln K_F$.

The Langmuir isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent, and is expressed in the following equation:

$$\frac{C_e}{Q_e} = \frac{b}{Q_0} + \frac{C_e}{Q_0}$$

Where, C_e is the equilibrium phenol concentration in the solution (mg/L), Q_e is the equilibrium phenol concentration on the adsorbent (mg/g), Q_0 is the maximum adsorption capacity of the phenol (forming a monolayer) per unit weight of adsorbent (mg/g), and b is a constant related to the affinity of the binding sites (L/mg).

The essential characteristics of the Langmuir isotherm can be expressed by a separation factor R_L , which is defined in the following equation:

$$R_L = \frac{1}{1+bC_0}$$

The R_L value shows the nature of the adsorption process to be unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

Phenol was examined at optimized condition $pH \sim 4.0 \pm 0.8$ for alginate stabilized AgNPs beads and $pH \sim 4.0 \pm 0.8$ for alginate stabilized AuNPs beads at contact time 25 hrs at room temperature.

The linearized Freundlich isotherm was applied for the system and shown in Fig. 10, and their parameter values were calculated and presented in Table 1. The observed values of K_F for phenol are 2.55 ± 0.78 and 6.54 ± 0.67 mg/g with alginate stabilized AgNPs and AuNPs beads respectively. The linearized Langmuir isotherm was applied for the system and shown in Fig. 11 and their parameter values were calculated and presented in Table 1. The observed values of Q_0

for phenol are 2.15 ± 0.87 and 2.25 ± 0.68 mg/g with alginate stabilized AgNPs and AuNPs beads respectively. The results obtained from adsorption isotherms, according to Freundlich and Langmuir models are shown in Table 1.

Freundlich values indicated high adsorption capacity of adsorbate on adsorbent as compared to the Langmuir isotherm model, which implied a significant affinity between the adsorbent and adsorbate in which adsorption is based on heterogeneous surface of adsorbents and Freundlich isotherm is not restricted to the formation of the monolayer [47]. In case of phenol the adsorption capacity was much faster when alginate stabilized AuNPs beads was the adsorbent as compared to alginate stabilized AgNPs beads. It is estimated from the adsorption experiments that loading of NPs in the case of alginate stabilized AuNPs beads is much high compared to alginate stabilized AgNPs beads [33].

Kinetic modeling

Kinetic investigations were carried out to measure the adsorption rate under various experimental conditions such as pH, initial concentration, and to determine the time required to reach adsorption equilibrium. The mixture (adsorbate + adsorbent) was shaken at a constant agitation speed at different time intervals. The calculation method of the adsorption of organic species was same as in adsorption equilibrium experiments.

Kinetic models are used to investigate the mechanism of adsorption and potential rate controlling steps which is helpful for selecting optimum operating condition for the full-scale batch process [48]. The adsorption kinetics was investigated by using pseudo-first-order and pseudo-second-order kinetic equations to test experimental data. Percentage removal of phenol at a fixed adsorbent dose was monitored with time. The kinetics of phenol removal by NPs beads indicated rapid binding of adsorbate to the adsorbent during first few min, followed by a slow

increase until a state of equilibrium was reached. No change in the uptake capacity was observed with further increase in equilibrium time. The initial rapid phase may be due to increased number of vacant sites available at the initial stage. As a result, there was an increased concentration gradient between adsorbate in solution and adsorbate on the adsorbent [49]. Generally, when adsorption involves a surface reaction process, the initial adsorption is rapid. Then, a slower adsorption would follow as the available adsorption site gradually decreases. Kinetics [50] of sorption was modelled by the pseudo-first-order equation and the pseudo-second-order equation [51] models at initial concentration.

The adsorption kinetics can be described by the pseudo-first-order kinetic model and the pseudo-second-order kinetic model [52-53]. The pseudo-first-order equation is generally expressed as following:

$$\left(\frac{1}{q_t}\right) = \left(\frac{k_1}{q_e}\right)\left(\frac{1}{t}\right) + \left(\frac{1}{q_e}\right)$$

The pseudo-second-order equation is expressed as follows:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{q_e^2 k_2}$$

Where, q_e and q_t are the equilibrium adsorption capacity (mg/g) and the adsorption capacity at time t , respectively; k_1 is the rate constant of pseudo-first-order adsorption (time^{-1}). k_2 is the rate constant of pseudo-second-order adsorption kinetic (g/mg/time). The plot of q_t vs t should give a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively. The plot is a linear relationship between t/q_t and t , q_e and k_2 can be determined from the slope and intercept of the plot of t/q_t vs t , respectively.

Figure 12 show plot for phenol of pseudo-first-order equilibrium. Figure 13 show plots for phenol of pseudo-second-order equilibrium. The correlation coefficients (R^2), adsorption capacity (q_e) and the rate constant of pseudo-first-order and pseudo-second-order for adsorbents are summarized in Table 2. For all the systems studied, good correlation coefficients were obtained by fitting the experimental data to pseudo-first-order and pseudo-second-order kinetics. But the adsorption kinetic data fitted best in pseudo-first-order model, where linear plot of t vs q_t was obtained. Pseudo-first-order values indicated high adsorption and correlation coefficients of adsorbates on adsorbents than pseudo-second-order, which can be ascribed to the effective physical adsorption of adsorbate onto adsorbents.

Desorption studies

A solute adsorbed on a material is normally desorbed by placing the saturated adsorbent in a solution without the solute. In this way, the solute adsorbed on the surface would be desorbed and diffused back to the solution. Desorption studies provide very useful information about the adsorption mechanism and procedure for regenerating the saturated adsorbent. Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the adsorbate. To make the adsorbent economically competitive, the prepared composite material should be reused for 'n' number of cycles.

To check the economic viability of this composite adsorbent desorption experiments were carried out. Water treatment will be economical if the adsorbent can be recovered and repeatedly used.

A $72.0 \pm 0.8\%$ and $90.0 \pm 0.8\%$ of the phenol was removed in the first cycle by alginate stabilized AgNPs and AuNPs beads, respectively. After this, the used adsorbents were treated with 100 mL of 0.05 N HNO_3 . For obtaining the reusability of the AgNPs and AuNPs beads

desorption cycle was repeated 20 times with the same adsorbent and the result are shown in Fig. 14. The removal of phenol decreased nominally per cycle up to 20 cycles suggesting high efficiency of the adsorbent. In the last cycle $62.0\pm0.8\%$ and $81.0\pm0.8\%$ alginate stabilized AgNPs and AuNPs beads of phenol by adsorptions were feasible. For obtaining the reusability of the adsorbent beads desorption cycle was repeated many times with the same adsorbent.

Comparison with other studies

A comparison of the advantage and disadvantage of the NPs with those of the other adsorbents reported in the literature is given in Table 3. The percentage removal of phenol is high and almost same by using activated carbon (AC), low-cost adsorbent, biosorbent and nanosorbent. The reusable capacity of NPs beads is relatively high than the other adsorbents reported. Thus, it may be considered that a good desorption performance of adsorbents is useful in the recovery of the removed phenol. This, again, adds to the economic viability of the system.

Conclusions

Phenol was effectively removed $72.0\pm0.8\%$ and $90.0\pm0.8\%$ from aqueous solutions using alginate stabilized AgNPs and AuNPs beads respectively as the adsorption process. Biopolymer calcium alginate gel beads were used as a template for NPs growth using a green microwave irradiation approach. The alginate served as both a reductant and a stabilizer. The surface morphology was characterized by SEM studies. The investigation on the formation of alginate stabilized AgNPs and AuNPs using UV-visible spectroscopy has shown the absorption peaks at 420 nm for AgNPs and at 520 nm for AuNPs. The experiments were performed with initial concentrations varying from 5–40 mg/L of phenol. The percentage removal increases with increase in contact time. The adsorption equilibrium was reached at about 25 hrs for phenol. The pH 4.0 ± 0.8 for phenol were found most favorable and at this pH the percentage removal is high

at room temperature (27 °C). Batch experiments demonstrated that a 2 g adsorbent dosage is capable of removing maximum amount of organic species from aqueous solution. The maximum adsorption capacity of alginate stabilized AgNPs beads and alginate stabilized AuNPs beads calculated from Freundlich isotherm model were 2.55 ± 0.78 mg/g and 6.54 ± 0.67 mg/g for phenol. The fitness of Freundlich isotherm model indicated the adsorption is based on heterogeneous surface of adsorbents and Freundlich isotherm is not restricted to the formation of the monolayer. The data on kinetic studies indicated that the adsorption kinetics of phenol on adsorbent beads followed the pseudo-first-order kinetics indicating physicosorptions. The regeneration of the spent adsorbent is easily performed with HNO_3 and the composite adsorbent can be effectively reused for 20 cycles of phenol consecutively. The percentage removal of phenol was high in low cost adsorbents but the efficiency of reusable capacity is not convinced. Although nanoparticles-based polymeric adsorbent is little expensive but it has long run reusable capacity. The nontoxicity of the adsorbent, its reusability and simple method of preparation are its added advantages making it an environment friendly material with potential to be used in water treatment. The adsorption efficiency of AuNPs beads was much higher towards phenol removal compared to that of AgNPs, as estimated from the adsorption experiments. Overall, alginate stabilized metal NPs showed excellent adsorptive characteristics for the removal of organic pollutants from aqueous solution.

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