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ORIGINAL ARTICLE

Microwave green synthesis of biopolymer-stabilized silver nanoparticles and their adsorption behavior for atrazine

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Abstract The application of silver nanoparticles for the removal of atrazine has been investigated. The silver nanoparticles beads were used as an adsorbent in the present study. Silver nanoparticles were prepared in the laboratory by a microwave irradiation method. The effect of initial concentration on the removal of atrazine was studied by varying the initial concentration of atrazine from 5 to 30 ppm. It was found that the percent removal of atrazine decreases on increasing the initial atrazine concentrations. A contact time of 14 h was found to be sufficient for maximum removal and was recorded as the equilibration time. The pH 6.0 ± 0.6 for atrazine was found most favorable and at this pH the percentage removal is high at room temperature (27 °C). Batch experiments demonstrated that a 2 gm adsorbent dosage is capable of removing maximum amount of atrazine from aqueous solution. Resulting data at room temperature were analyzed by the Freundlich and Langmuir models using linearized equations. Resultant data were analyzed by pseudo-first-order and pseudo-second-order rate equations. Desorption studies were made to elucidate recovery of the adsorbate and adsorbent for the economic competitiveness of the removal system. Findings of the present study revealed that silver nanoparticles beads can be an effective adsorbent for the removal of atrazine from aqueous solution.

Keywords Microwave irradiation · Silver nanoparticles · Pesticide · Green synthesis

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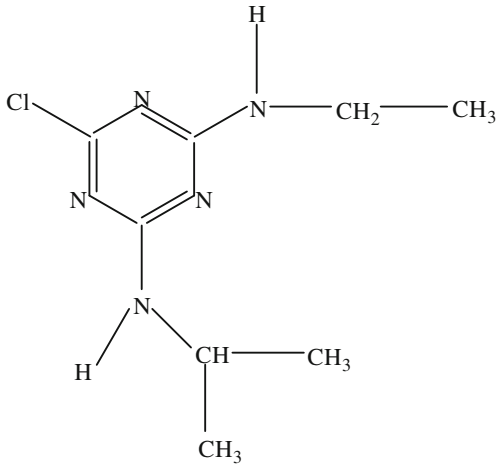
Introduction

The intensive use of pesticides in agriculture has generated contamination of groundwater and surface waters. The presence of pesticides in water can cause serious environmental and human health problems. Atrazine [2-chloro-4-(ethylamino)-6-isopropylamine-s-triazine] (Fig. 1) is one of the most widely used pesticides. Atrazine kills weeds in corn (*Zea mays* L.) and sorghum (*Sorghum bicolour* L.) fields by inhibiting photosynthesis. According to Battaglia (1989) it constitutes a priority pollutant of water. Atrazine has been detected in groundwater, in surface water and in precipitation throughout the United States and even in rainfall and fog (Schottler et al. 1994). In surface water, atrazine affects aquatic plants. A number of methods have been reported for the removal of pesticides from waste waters (Brown et al. 2004; Chaparadza and Hossenlopp 2012; Danish et al. 2010; Boussahel et al. 2000; Paknikar et al. 2005). Photochemical or chemical treatments are often inefficient for the removal of synthetic organochlorine pesticides from waters. The adsorption process is considered to be superior to other techniques (Bajpai et al. 2004; Shah et al. 2012; Ramos et al. 2011; Pal and Deb 2012a, b; Pal and Deb 2013; Pal et al. 2013; Xiong et al. 2010; Hou et al. 2011; Mukherjee et al. 2007; Djebbar et al. 2012; Bhattacharyya and Sarma 2003; Belhachemi and Addoun 2011; Chowdhury and Saha 2012). Table 1 shows some of the comparative features on different adsorbents



2-chloro-4-(ethylamino)-6-isopropylamine-s-triazine

Fig. 1 Chemical structure of atrazine

Table 1 Comparative features of some reported adsorbents

S. No.	Adsorbents	Advantage	Disadvantage	References
1	AC	High adsorption capacity and versatility	Quite expensive, greater the cost	(Babel and Kurniawan 2003)
2	Low-cost adsorbent	Abundant in nature, inexpensive, require little processing, effective materials	Low cost may compensate for the associated drawbacks	(Babel and Opiso 2007)
3	Biosorbent	High selectivity, efficiency, cost effectiveness and good removal performance	Effective but favorable condition	(Shah et al. 2012)
4	Nanosorbent	Stable, efficient, eco-friendly, easy to prepare and recyclable	Little expensive but long run reusable	Present work

reported earlier. The advanced water treatment processes and mainly the adsorption onto activated carbon (AC) have proved to be the most efficient and reliable method for the removal of water soluble organic pesticides. However, this technique has some disadvantages such as rapid saturation of carbon filters resulting in decreased efficiency towards elimination of pollutants due to competitive adsorption from natural organic matters (Babel and Kurniawan 2003). In recent years, the deposition of metal nanoparticles (NPs) on various substrates has attracted considerable interest (Tang et al. 2007; Siboni et al. 2011; Jha and Prasad 2011). In this way, metal NPs can be dispersed homogeneously on the surface of the substrates and therefore the fraction of surface atoms becomes large. This has made possible to use metal NPs and their assemblies due to the influence of the surface structure for several applications (Tang et al. 2007). Amongst them, much attention has been paid to silver nanoparticles (AgNPs) because of its low absorption in the optical region and a narrow plasmon resonance band in comparison to the other metal nanoparticles (Mulvany 1996; Oldenburg et al. 1998).

In this work, we report an adsorbent derived from AgNPs beads for atrazine removal from aqueous solution. The effects of factors such as initial concentration, contact time, pH and adsorbent dose were investigated. In addition, the equilibrium isotherms, adsorption kinetics and desorption studies of atrazine onto the alginate-stabilized AgNPs beads were also investigated.

Experimental section

Materials

Atrazine was obtained from the Gramoxone (India). Silver nitrate ($AgNO_3$) was purchased from Merck (India). Sodium alginate was obtained from LOBA (India). Calcium chloride ($CaCl_2$) was obtained from Qualigens (India). Triple distilled water was used throughout the experiments.

Measurements

A Samsung CE2877 domestic microwave oven (850W), Samsung Electronics Ltd, New Delhi, India, was employed for irradiating solutions. The surface morphology of the adsorbents was examined by a JEOL-JSI, model No-5600, scanning electron microscopy (SEM). Absorption spectra were recorded in a Varian Carry 50 UV–visible spectrophotometer equipped with a peltier temperature controller unit. The XRD measurements were carried out using (Bruker D8 Advance) X-ray diffractometer. FTIR spectra of the adsorbent were recorded on IR Affinity-1, Shimadzu spectrophotometer.

Preparation of AgNPs beads

The AgNPs beads employed as adsorbent were prepared in two steps. In the first step, a homogenous reaction solution was prepared by dissolving 0.2 mol/L sodium alginate and 1.0×10^{-4} mol/L $AgNO_3$ using triple distilled water in a 50-mL conical flask. Then, the flask was placed on the turntable of the microwave oven and the mixture was irradiated at a power of 300 W for the duration of 4 min.

Fig. 2 A photograph showing alginate-stabilized AgNPs beads

The reaction was allowed to occur intermittently to prevent any increase of pressure. After irradiation, the colloidal solution having pale yellow color was cooled to room temperature and stored for its characterization. In the second step, the above prepared AgNPs in solution was added drop wise into a 0.1 M $CaCl_2$ solution with the help a syringe and under constant stirring to produce beads of AgNPs. The beads so produced were allowed to harden by leaving them in $CaCl_2$ solution for 10 min and thereafter filtered and washed with triple distilled water. These AgNPs beads were stored in triple distilled water at room temperature and used as such. A photograph of AgNPs beads is shown in Fig. 2 (Pal and Deb 2013).

Adsorption experiments

A standard solution of atrazine containing 5 mg/L was used for batch studies. Batch experiments were conducted in 250-mL conical flask in which 100 ml of atrazine containing water and 2 gm of AgNPs beads were poured. The suspension was shaken in a rotary shaker. After shaking, the suspension was centrifuged and the amount of atrazine in supernatant was examined UV–visible spectrophotometrically at a wavelength of 230 nm. The percentage removal of atrazine was calculated by the following equation

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

where C_i and C_e are initial and equilibrium concentrations (mg/g) of atrazine solution, respectively.

Desorption studies

In order to desorb the atrazine, the AgNPs beads loaded with atrazine were exposed to 0.05 N HNO_3, centrifuged and washed with triple distilled water. The AgNPs beads were then again exposed to 0.05 N HNO_3 to strip any remaining atrazine and then reused. In order to show the reusability of adsorbent beads an adsorption–desorption cycle of atrazine was repeated 26 times by the same process. The percentage desorption of atrazine was estimated from the following equation:

$$\text{Percentage desorption} = \frac{\text{amount of atrazine liberated by acid}}{\text{amount of atrazine adsorbed on adsorbent}} \times 100$$

.

Results and discussion

Characterization of the AgNPs

SEM studies on alginate-stabilized AgNPs beads were performed to gain information about the particle morphologies. The closely packed AgNPs beads are shown in Fig. 3a. The UV–visible spectrum of AgNPs is shown in Fig. 3b. The colloidal silver solution exhibits a strong absorption at 420 nm. Thus, the pale yellow color of the colloidal silver sample provides clear evidence for the formation of AgNPs. The structure of the prepared AgNPs was characterized by X-ray diffraction (XRD) as shown in Fig. 3c. The average size of the particles can be derived from the peak width using the Scherrer equation,

$$d = \frac{0.9\lambda}{B\cos\theta}$$

where, d corresponds to the particle size, λ is the X-ray wavelength, θ is the Bragg's angle and B corresponds to the full width at half maximum (fwhm) of the peak under consideration. At angle 2θ is 36.88, 39.37, 43.02, 47.42, 56.58 and the corresponding particles size is 6.28, 6.28, 6.34, 6.41, 6.70 nm respectively for AgNPs. Thus, the AgNPs mean size is estimated to be 7 nm. Figure 3d shows the corresponding particle size distribution histogram of the AgNPs. The size distribution histogram reveals that such AgNPs range from 5–8 nm in size. About 50 % of these NPs consist of particles with 6 nm diameter, 10 % particles were of 8 nm size and size of the remaining particles was in the range of 5, 7 nm diameter. The FTIR spectra of bare and atrazine-adsorbed AgNPs beads are shown in Fig. 3e. The spectra clearly mark the presence of ~1,400 and ~1,530/cm; those are due to the symmetric and antisymmetric stretching vibrations of $-COO^-$, respectively. The (COO^-) band of silver calcium alginate was found at ~1,385/cm. More importantly, a new peak appeared in the region at 416/cm indicating the presence of C–C bending vibration.

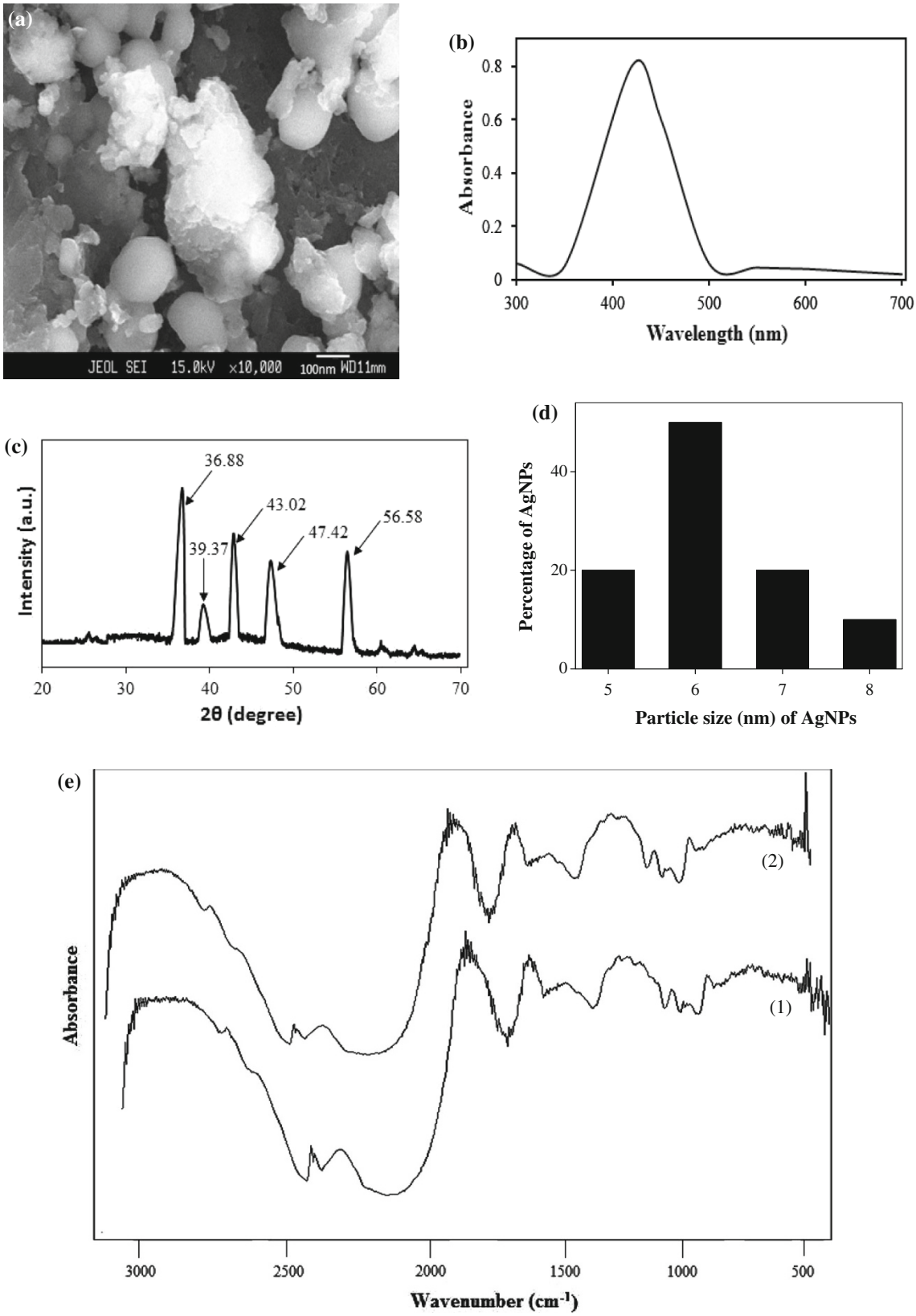


Fig. 3 **a** SEM image of alginate-stabilized AgNPs beads, **b** UV–visible spectrum of the synthesized AgNPs, **c** XRD diffraction pattern for AgNPs, **d** size distribution of the AgNPs synthesized under optimum experimental conditions, **e** FTIR spectra of (1) AgNPs beads and (2) atrazine-loaded AgNPs beads

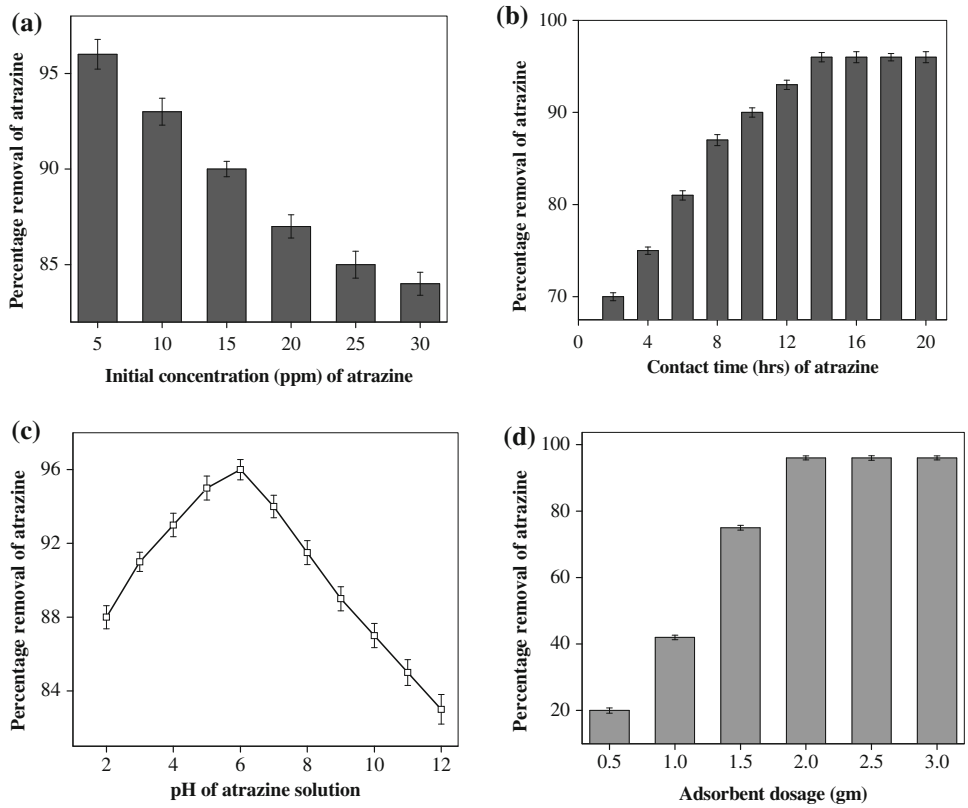


Fig. 4 **a** Effect of initial concentration, **b** effect of contact time, **c** effect of pH, **d** effect of dose on the removal of atrazine by alginate-stabilized AgNPs beads at room temperature (with *error bars*)

Initial concentration effect of atrazine

The effect of initial concentration on atrazine removal using AgNPs beads is shown in Fig. 4a with error bars showing the values of standard deviation ($n = 5$). The experiment was conducted at pH 6.0 ± 0.6 at room temperature. In this figure, it has been shown that when the atrazine concentration was increased from 5 to 30 mg/L, the percentage removal of atrazine decreased from 96.0 ± 0.8 to 84.0 ± 0.7 % by alginate-stabilized AgNPs beads. The percentage removal decreases with an increase at the initial concentration. The decrease in the percentage removal of atrazine can be explained by the fact that the AgNPs beads had limited active sites, which would have become saturated above a certain concentration.

Effect of contact time

For the investigation of the effect of contact time on atrazine removal by alginate-stabilized AgNPs beads experiments were conducted in the initial concentration 5 mg/L for adsorbent dosage 2 gm at room temperature. The effect of contact time on atrazine removal by AgNPs beads is shown in Fig. 4b with error bars showing the values of standard deviation ($n = 5$). For a contact time period between 2 and 14 h, the percentage removal of atrazine was 70.0 ± 0.4 to 96.0 ± 0.8 %. As shown in Fig. 4b, the percentage removal of atrazine increases with extended contact time and attains equilibrium at about 14 h. Therefore, the time of equilibrium was 14 h for the present system. It is clear from this figure that the removal of atrazine is significantly rapid in the initial stages, due to availability of more than required number of active sites on the surface of AgNPs beads, which becomes slower at the later stages of contact time, due to the decreased or lesser number of active sites (Kannan and Karrupasamy 1998).

Effect of pH

The removal of atrazine by alginate-stabilized AgNPs beads was observed over a pH range of 2–12, as shown in Fig. 4c 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 atrazine was fixed at 6.0 ± 0.6 for AgNPs beads. Therefore, removal due to pH change alone may be due to the structural changes being affected in the adsorbate molecules (Mall et al. 2005).

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 gm in 100 mL aqueous solution of atrazine (5 mg/L) at room temperature for equilibrium time. The results are shown in Fig. 4d for atrazine. It is evident from the plots that the percentage removal of atrazine from the aqueous solution increases with increase in the adsorbent dosage. It was observed that the removal efficiency increased from 20.0 ± 0.8 to 96.0 ± 0.8 % for atrazine with the adsorbent dose varying from 0.5 to 2 gm of alginate-stabilized AgNPs beads and thereafter it reached a constant value. 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 atrazine adsorbed.

Adsorption isotherm

To examine the relationship between adsorbed amount of atrazine and equilibrium concentration, sorption isotherm models are widely employed for fitting the data, of which the Freundlich and Langmuir equations are most widely used.

Freundlich isotherm

The Freundlich isotherm model of adsorption of atrazine from aqueous medium equation can be lineralized from the equation:

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

where, K_F and n are Freundlich constant, characteristics of the system indicating the adsorption capacity and adsorption intensity, respectively. K_F is the predicted quantity of adsorption per gram of the AgNPs beads at unit equilibrium concentration of atrazine solution and $1/n$ is the measure of the nature and strength of the adsorption process and the distribution sites.

Langmuir isotherm

The Langmuir isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent (Gibson and Argo 1918), and is expressed in the following equation:

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

where, C_e is the equilibrium concentration in the solution (mg/L), Q_e is the equilibrium concentration on the adsorbent (mg/g), Q_o is the maximum adsorption capacity (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 (Hall et al. 1966), which is defined in the following equation:

$$R_L = \frac{1}{1 + bC_O}.$$

The R_L value shows the nature of the adsorption process to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). Table 2 shows that R_L values obtained at room temperature were in the range 0–1, indicating that the experimental conditions in this work were favorable for the adsorption process (Eftekhari et al. 2010).

Atrazine was investigated at optimized condition pH ~6.0 ± 0.6 for alginate-stabilized AgNPs beads at contact time 14 h at room temperature. The linearized Freundlich isotherm was applied for the system and shown in Fig. 5a for atrazine and their parameter values were calculated and presented in Table 2. The observed value of K_F for atrazine is 1.823 ± 0.710 mg/g with alginate-stabilized AgNPs beads. The linearized Langmuir isotherm was applied for the system and shown in Fig. 5b for atrazine and their parameter values were calculated and presented in Table 2. The observed value of Q_o for atrazine is 1.569 ± 0.780 mg/g with alginate-stabilized AgNPs beads. The results obtained from adsorption isotherms according to Freundlich and Langmuir models are shown in Table 2.

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 (Mohammadi et al. 2011).

Kinetic modeling

Adsorption kinetic models are important in the process of the removal of atrazine from aqueous solutions. To understand the mechanism of adsorption and potential rate-controlling step, the adsorption kinetics was investigated using pseudo-first-order and pseudo-second-order kinetic equations to test experimental data.

Pseudo-first-order model

The pseudo-first-order model can be expressed by following equation: (Dogan et al. 2007)

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

where, q_e and q_t (mg/g) are the amount of adsorbed atrazine on the adsorbent at equilibrium and at time t,

Table 2 The isotherm parameters and correlation coefficients of Freundlich and Langmuir models

Adsorbate	Adsorbent	Freundlich constants			Langmuir constants			
		K_F (mg/g)	n	R^2	Q_o (mg/g)	b (L/mg)	R^2	R_L
Atrazine	AgNPs	1.823 ± 0.710	1.956	0.999	1.569 ± 0.780	0.6151	0.9499	0.2454

K_F adsorption capacity, n adsorption intensity, R^2 correlation coefficients, Q_o maximum adsorption capacity (mg/g), b constant related to the affinity of the binding sites (L/mg), R_L nature of the adsorption process

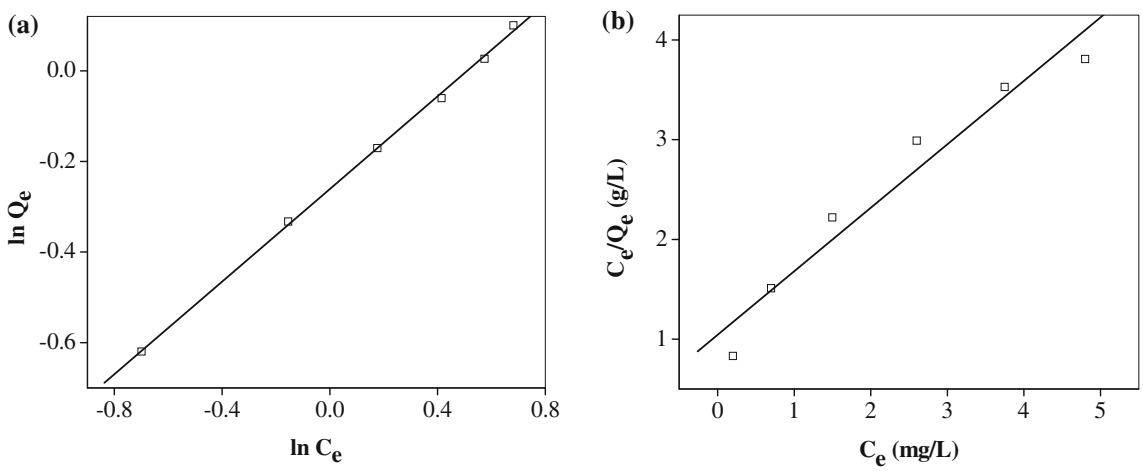


Fig. 5 **a** Freundlich isotherm plot and **b** Langmuir isotherm plot for adsorption of atrazine on alginate-stabilized AgNPs beads at room temperature

respectively. k_1 (per hour) is the rate constant of the first-order-kinetic equation. The values of k_1 were obtained from the linear plots of $1/q_t$ versus $1/t$ at room temperature and q_e from the intercept.

Pseudo-second-order model

The adsorption data were also analyzed by a pseudo-second-order kinetic equation. The pseudo-second-order model can be expressed as follows: (Dogan et al. 2007)

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

where, k_2 (g/mg/hr) is the rate constant of the pseudo-second-order equation. The values for q_e and k_2 can be determined from the slope and intercept of the straight line of the plot t/q_t versus t, respectively. The values of pseudo-first-order and pseudo-second-order rate constants for the removal of atrazine by adsorption on alginate-stabilized AgNPs beads at room temperature were calculated from the straight line plots of Fig. 6a, b. 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 3. 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 $1/t$ vs $1/q_t$ was obtained. Pseudo-first-order values indicated high adsorption of adsorbates on adsorbents than pseudo-second-order values, which can be ascribed to the effective physical adsorption of absorbate onto adsorbents.

Comparative study of the adsorption capacity of AgNPs and conventional adsorbents

Desorption studies help to clarify the mechanism of adsorption and recovery of the adsorbate and adsorbent; 96.0 ± 0.8 % of the atrazine was removed in the first cycle. The used adsorbent was treated with 0.05 N HNO_3 which resulted in 99 % stripping of atrazine. For obtaining the reusability of the AgNPs beads desorption cycle was repeated 26 times with the same adsorbent and the result is shown in Fig. 7. The removal of atrazine decreased nominally per cycle up to 26 cycles suggesting high efficiency of the adsorbent. In the last cycle 76.0 ± 1.4 % of atrazine was removed. A comparison of the advantage and disadvantage of the AgNPs beads with those of the other adsorbents reported in the literature is given in Table 1. The percentage removal is high and almost same for adsorbates such as activated carbon (AC), low-cost adsorbent, biosorbent and nanosorbent but the reusable capacity

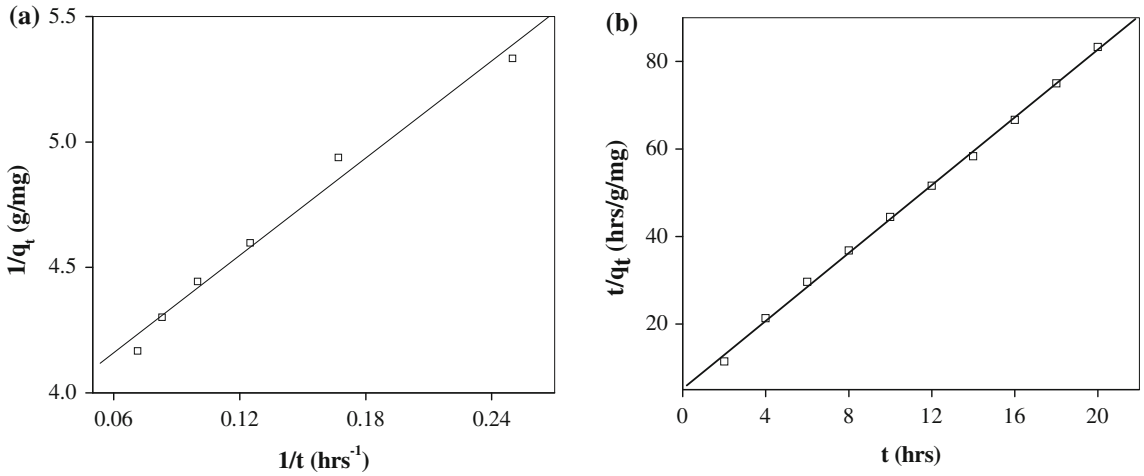


Fig. 6 **a** Pseudo-first-order kinetic plot and **b** pseudo-second-order kinetic plot for the removal of atrazine by alginate-stabilized AgNPs beads

Table 3 Adsorbents value calculated using the pseudo-first-order model and pseudo-second-order model for the adsorption of atrazine

Adsorbate	Adsorbent	Pseudo-first-order model			Pseudo-second-order model		
		q_e (mg/g)	k_1 (per hour)	R^2	q_e (mg/g)	k_2 (g/mg/hr)	R^2
Atrazine	AgNPs	0.3651 ± 0.5040	1.713	0.9830	0.2578 ± 0.6510	2.892	0.9987

k_1 pseudo-first-order rate constant, k_2 pseudo-second-order rate constant, q_e adsorption capacity, R^2 correlation coefficient

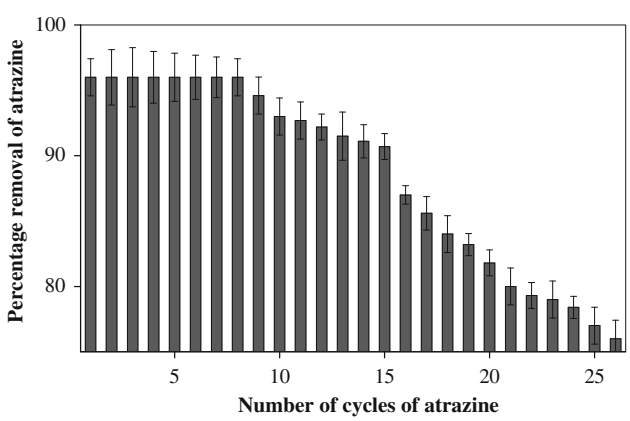


Fig. 7 Percentage removal of atrazine by alginate-stabilized AgNPs beads after desorption ($n = 5$)

of NPs beads is relatively high when compared with the other adsorbents reported, namely, AC, sawdust and so forth (Table 1). Thus, it may be considered that a good desorption performance of adsorbents is useful in the recovery of the removed adsorbate. This, again, adds to the economic viability of the system.

Conclusions

Alginate-stabilized AgNPs beads have proved to be abundant and highly efficient materials for atrazine removal from aqueous solution by batch method. The AgNPs beads were capable of removing 96.0 ± 0.8 % of atrazine at room temperature. 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 using UV–visible spectroscopy has shown the absorption peaks at 420 nm. The average size of AgNPs is about 7 nm as observed via XRD technique. The adsorption equilibrium was reached at about 14 h. The pH 6.0 ± 0.6 was found most favorable and at this pH the percentage removal is high at room temperature (27 °C). Batch experiments demonstrated that a 2 gm adsorbent dosage is capable of removing maximum amount of atrazine from aqueous solution. The maximum adsorption capacity of alginate-stabilized AgNPs beads calculated from Freundlich isotherm model was 1.823 ± 0.710 mg/g for atrazine. The isothermal data obey the Freundlich model better compared to Langmuir model for the adsorption of atrazine. The data on kinetic studies indicated that the adsorption kinetics of atrazine on adsorbent beads followed the pseudo-first-order kinetics indicating physicosorption process. The regeneration of the spent adsorbent is easily performed with HNO_3 and the composite adsorbent can be effectively reused for 26 cycles consecutively. Nanoparticles-based polymeric adsorbent is little expensive but it has long run reusable capacity. The AgNPs beads' adsorbents were more efficient

than most of the reported adsorbents. The non-toxicity 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. Overall, alginate-stabilized AgNPs showed excellent adsorptive characteristics for the removal of atrazine from aqueous solution. The AgNPs beads' adsorbents were more efficient than most of the reported adsorbents.

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