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# Fast and efficient removal of silver (I) from aqueous solutions using aloe vera shell ash supported $Ni_{0.5}Zn_{0.5}Fe_2O_4$ magnetic nanoparticles

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Abstract: Silver (I) was removed from aqueous environment by aloe vera shell ash supported  $Ni_{0.5}Zn_{0.5}Fe_2O_4$  magnetic nanoparticles. The adsorbent was characterized by several methods including X-ray diffraction (XRD), scanning electron microscopy (SEM), BET isotherm, vibrating sample magnetometer (VSM) and Fourier transform infrared spectroscopy (FT-IR). To determine the absorption of silver (I) by this adsorbent, different pH values (2–7), adsorbent dose (0.01–0.5 g), concentrations of Ag<sup>+</sup> (50, 100, 200, 300, 500, 700 and 1000 mg/L) and exposure time (5–100 min) were experimented. The highest removal efficiency of Ag<sup>+</sup> was achieved under optimum condition (30 min and pH=5). The optimum adsorbent dose was 0.20 g (in 50 mL of 100 mg/L Ag<sup>+</sup> solution), which achieved a removal efficiency of 98.3%. The maximum monolayer adsorption capacity based on the Langmuir isotherm is 243.90 mg/g. Characterization results revealed that specific surface area and porous volume were 814.23 m<sup>2</sup>/g and 0.726 cm<sup>3</sup>/g, respectively. The experimental data were fitted well with the Langmuir and Freundlich isotherm models. Synthesized adsorbent has desired surface area and adsorptive capacity for silver (I) adsorption in aquatic environment.

**Key words:** adsorption;  $Ag^+$  ions;  $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ; aloe vera

#### **1** Introduction

Heavy metals as raw materials or catalysts are used extensively in many industrial processes, such as mining, metallurgy, electrolysis, electroplating and leather [1]. They can be afterward discharged into the environment via wastewater, which has become a hazard to human and local environment [2]. Because the heavy metals in water are difficult to be bio-degenerated and tend to cumulate in living structures through the food chain [3]. the wastewater including heavy metals should be cleaned up before evacuation. Wastewater comprising heavy metals is usually cleaned up via precipitation, membrane separation, ion exchange, and adsorption [4-7]. Among them, adsorption was established as an important and economically practical treatment technology for removing the Ag<sup>+</sup> ions from water and wastewater. Activated carbon is usually used adsorbent for the removal of Ag<sup>+</sup> ions from aqueous solution. Despite the abundance applications of activated carbon, its use is sometimes limited due to its high cost and also for loss during its re-formation [8-10]. Therefore, the researchers are on the search for new low-cost substitute adsorbents for the water pollution control, especially, where cost acts an important role. Much effort has been done towards the development of another adsorbents that are effective and low-cost. They can be produced from a wide diversity of raw materials, which are abundant and have high carbon and low inorganic content. Owing to the low cost and high accessibility of these materials, it is not essential to have complex regeneration processes. Such low cost adsorption methods have attracted many researchers. Often, the adsorption capabilities of such adsorbents are not large, therefore, the study and investigation of more and more new adsorbents are still under development. Several common adsorbents of different origin, primarily including activated carbons, clays, zeolites, biomass, and polymeric materials, have been used for the removal of heavy metal from the industrial wastewater [11-15]. In recent years, due to economic problems, creating a cheap and efficient alternative method of wastewater treatment instead of expensive and inefficient methods is of great importance. One of the most efficient, technical and economic methods in this context, is the use of magnetic adsorbent. These adsorbents have magnetic properties and by using an external magnetic field they can be

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easily separated from the solution. In the magnetic high costs of separation, such separation, centrifugation and filtration are not included [16]. Extensive researches in the field of magnetization of materials such as chitosan [17], silica [18], polymer [19] and activated carbon [20] have been conducted for water contaminants removal. The use of this property in the nanoparticles, due to their high specific surface area and adsorption capacity is very good [21-23]. Nickel-zinc ferrites have drawn noticeable consideration of researchers as a result of their remarkable magnetic properties, large permeability, and very high electrical resistivity [24]. They have extensive potential applications such as high-density information storage devices, microwave devices, transformer cores, and magnetic fluids [25]. The use of activated carbon to remove chlorine, separating gases and air pollution treatment, recycling of heavy metals from aqueous solutions has many applications. But because of the high cost, other options have been suggested as an alternative. Ash due to the low cost of production is a good alternative to activated carbon [26-30]. Ashes can be produced from a wide range of carbon materials, such as wood, coal, shell, walnut shell, fruit stones, and agricultural waste [31].

In this work, we became interested to investigate the capability of the surface modified  $Ni_{0.5}Zn_{0.5}Fe_2O_4$  magnetic nanoparticles with ash prepared from aloe vera shell ( $Ni_{0.5}Zn_{0.5}Fe_2O_4/ASA$ ) as a low-cost adsorbent for removal of  $Ag^+$  ions from aqueous solution and also to study the adsorption mechanism of  $Ag^+$  ions onto this adsorbent. For this purpose, a set of batch adsorption experiments (pH, contact time, adsorbent dosage and initial  $Ag^+$  ions concentration) on the  $Ag^+$  ions removal using this adsorbent were carried out at optimum conditions. The characterization of the adsorbent was described by FT-IR, XRD and SEM analyses.

#### 2 Experimental

#### 2.1 Materials and methods

Analytical-grade salt AgNO<sub>3</sub> was obtained from Merck. A 1000 mg/L stock solution of the salt was prepared in deionized water. All working solutions were prepared by diluting the stock solution with deionized water. Deionized water was prepared using a Millipore Milli-Q (Bedford, MA) water purification system. All reagents (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, NaOH and HNO<sub>3</sub>) used in the study were of analytical grade and purchased from Aldrich. Before each experiment, all glassware were cleaned with dilute nitric acid and repeatedly washed with deionized water. X-ray diffraction analysis (XRD) was carried out using a PAN analytical X'Pert Pro X-ray diffractometer. Surface morphology and particle size were studied using a Hitachi S–4800 SEM instrument. FT-IR spectra were determined as KBr pellets on a Bruker model 470 spectrophotometer. The specific surface ( $S_{BET}$ ) of Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>/ASA was determined by a micrometrics apparatus (Gemini 2375) by adsorption of nitrogen at 77 K according to the traditional method of Brunauer Emmet and Teller or BET.

All the metal ion concentrations were measured with a Varian AA240FS atomic absorption spectrophotometer.

#### 2.2 Synthesis of aloe vera shell ash (ASA)

Aloe vera is grown in southern Iran. Aloe vera shells were collected from, Qeshm Island, Hormozgan, Iran, and were applied as a raw material for the preparation of surface modified adsorbent. The collected aloe vera shells were washed and dried in an air oven at 80 °C for 24 h and then ground and sieved to the desired particle size (2–3 mm). The resultant sieved powder was carbonized in a furnace at 700 °C at heating rate of 10 °C/min for 2 h. The methods for producing carbon materials are similar to other studies also have been used [26].

#### 2.3 Synthesis of Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>/ASA

At first, Ni–Zn ferrite was prepared using stoichiometric ratios of metal nitrates to freshly extracted egg-white [32]. The metal nitrates (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) and 2 g ASA were dissolved together in a minimum amount of double distilled water to get a clear solution. 60 mL of extracted egg-white dissolved in 40 mL of double distilled water while vigorous stirring, was added to nitrate mixture at ambient temperature. After constant stirring for 30 min, the resultant sol–gel was evaporated at 80 °C until dry precursor was obtained. The dried precursors were ground and calcined in a muffle furnace at 550 °C for 2 h.

#### 2.4 Adsorption experiments

Batch adsorption of silver ions onto the adsorbent  $(Ni_{0.5}Zn_{0.5}Fe_2O_4/ASA)$  was investigated in aqueous solutions under various operating conditions viz pH 2-7, at a temperature of 298 K, for an initial Ag<sup>+</sup> ion concentration of 100 mg/L. About 0.20 g adsorbent was added to 50 mL of silver nitrate solution (100 mg/L). Then, the mixture was agitated on a shaker at 250 r/min. The initial pH values of the silver solutions were adjusted from 2 to 7 with 0.1 mol/L HNO3 or 0.1 mol/L NaOH solutions using a pH meter. After equilibrium, the samples were centrifuged and the adsorbent (Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>/ASA) was removed magnetically from the solution. The Ag<sup>+</sup> concentration and final pH in the

supernatant were measured by flame atomic absorption spectrometer and a pH meter, respectively. The effects of several parameters, such as contact time, initial concentration, pH and adsorbent dose on extent of adsorption of  $Ag^+$  were investigated. Each datum point was taken as the average of three measurements.

The  $Ag^+$  removal rate (*R*) was calculated as

$$\eta = \frac{c_0 - c_t}{c_0} \times 100\% \tag{1}$$

where  $c_0$  and  $c_t$  (mg/L) are the concentrations of Ag<sup>+</sup> in the solution at initial and equilibrium time, respectively.

The amount of  $Ag^+$  adsorbed ( $Q_e$ ) was calculated using

$$Q_{\rm e} = \frac{(c_0 - c_{\rm e})V}{m} \tag{2}$$

where  $c_e$  is the equilibrium concentration of Ag<sup>+</sup> (mg/L), *m* is the mass of adsorbent (g), and *V* is the volume of solution (L).

To specify the regeneration of the adsorbent  $(Ni_{0.5}Zn_{0.5}Fe_2O_4/ASA)$  sample, adsorption/desorption cycles were repeated 5 times using the same adsorbent sample. Na<sub>4</sub>-EDTA (0.1 mol/L) was used as a desorption agent. Adsorbent  $(Ni_{0.5}Zn_{0.5}Fe_2O_4/ASA)$  samples carrying 99.95 mg/g Ag<sup>+</sup> were placed in this desorption medium (25 mL) and stirred magnetically at 25 °C for 1 h. After 1 h, the aqueous phase was separated from the adsorbent and the concentration of Ag<sup>+</sup> in that phase was measured.

#### 2.5 Adsorption isotherms

Adsorption isotherms were obtained by using 0.20 g of adsorbent and 50 mL of silver nitrate solution with different concentrations (50–1000 mg/L) at 298 K. These solutions were buffered at an optimum pH (pH=5) for adsorption and agitated on a shaker at 250 r/min until they reached adsorption equilibrium (30 min). The quantity of  $Ag^+$  adsorbed was derived from the concentration change.

#### **3** Results and discussion

## 3.1 Characterization of Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>/ASA magnetic nanoparticles

 $Ni_{0.5}Zn_{0.5}Fe_2O_4$  nano-crystallites were prepared according to the reported procedure by GABAL et al [32].  $Ni_{0.5}Zn_{0.5}Fe_2O_4/ASA$  nanocrystallites were characterized by FT-IR (Fig. 1), XRD (Fig. 2) and SEM (Fig. 3). FT-IR spectra of  $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ,  $Ni_{0.5}Zn_{0.5}-Fe_2O_4/ASA$  and ASA are compared in Fig. 1. In the FT-IR spectrum of  $Ni_{0.5}Zn_{0.5}Fe_2O_4/ASA$  (Fig. 1(a)), most of the bands of  $Ni_{0.5}Zn_{0.5}Fe_2O_4$  (Fig. 1(c)) and ASA (Fig. 1(b)) with a slight shift for some of them, are



Fig. 1 FTIR spectra of  $Ni_{0.5}Zn_{0.5}Fe_2O_4/ASA$  (a), ASA (b), and  $Ni_{0.5}Zn_{0.5}Fe_2O_4(c)$ 



Fig. 2 XRD patterns of  $Ni_{0.5}Zn_{0.5}Fe_2O_4$ : (a) Synthesized  $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ; (b) Standard  $Ni_{0.5}Zn_{0.5}Fe_2O_4$  (JCPDS 08–0234)



Fig. 3 SEM image of  $Ni_{0.5}Zn_{0.5}Fe_2O_4/ASA$  nanocomposite

observable, which shows that ASA has been supported well on the  $Ni_{0.5}Zn_{0.5}Fe_2O_4$ . The bands are in the low-frequency region (1000–500 cm<sup>-1</sup>) due to iron oxide skeleton, which is in agreement with the magnetite spectrum. The peak at 1444.85 cm<sup>-1</sup> showed the existence of Fe—O [33]. In Fig. 1(a), the presence of —OH stretching mode is evident by the peak close to 3446.75 cm<sup>-1</sup>. To confirm the Ni ferrite formation in the synthesized magnetic nanoparticles, the XRD spectrum of the sample was studied. The XRD patterns (Fig. 2) show that  $Ni_{0.5}Zn_{0.5}Fe_2O_4$  nanoparticles have the spinel structure, with all the major peaks matching the standard pattern of bulk  $Ni_{0.5}Zn_{0.5}Fe_2O_4$  (JCPDS 08–0234). The particle size of adsorbent was investigated by SEM. The SEM photograph of sample (Fig. 3) shows that average size of  $Ni_{0.5}Zn_{0.5}Fe_2O_4$ /ASA is approximately less than 100 nm.

The magnetic properties of the  $Ni_{0.5}Zn_{0.5}Fe_2O_4/ASA$  were evaluated by a vibrating sample magnetometer (VSM). As shown in Fig. 4, the saturation magnetic moments of the  $Ni_{0.5}Zn_{0.5}Fe_2O_4/ASA$  reached about 17 kA/m. It showed superparamagnetic behavior that would enable easy recovery of the adsorbent from solution under an applied magnetic field.



Fig. 4 VSM curve of  $Ni_{0.5}Zn_{0.5}Fe_2O_4/ANSA$  at room temperature

Some properties of the  $Ni_{0.5}Zn_{0.5}Fe_2O_4/ASA$  are presented in Table 1. The  $Ni_{0.5}Zn_{0.5}Fe_2O_4/ASA$  has a surface area about 814.23 m<sup>2</sup>/g and a porous volume equal to 0.726 cm<sup>3</sup>/g.

Specific surface area/ $(m^2 \cdot g^{-1})$	Porous volume/(cm <sup>3</sup> ·g <sup>-1</sup> )	Water content/%	
814.23	0.726	Trace	

# **3.1** Adsorption and removal of Ag<sup>+</sup> from aqueous solution

#### 3.1.1 Effect of contact time

The effect of contact time on the amount of silver adsorbed was studied at 100 mg/L initial concentration of silver. It could be observed from Fig. 5 that with the increase of contact time, the adsorption also increased. Minimum adsorption was 90.0% for 5 min and maximum adsorption value was 97.0% for 30 min. The adsorption characteristic indicated a rapid uptake of the silver. The adsorption rate, however, reduced to a constant value with an increase in contact time because all available sites were covered, and no active site was present for adsorbing.



**Fig. 5** Effect of contact time on removal efficiency (initial concentration=100 mg/L, pH=7, adsorbent dose=4 g/L and *T*= 298 K)

#### 3.1.2 Effect of pH

The acidity of the aqueous solution applies a considerable effect on the adsorption process because it can affect the solution chemistry of contaminants and the state of functional groups on the surface of adsorbents [34–36]. The effect of solution pH on Ag<sup>+</sup> adsorption was studied at pH 2–7 at 298 K. As shown in Fig. 6, the adsorption rate of Ag<sup>+</sup> is enhanced with increasing pH from 2 to 7. However, at low pH values, hydrogen ions (H<sup>+</sup>) are likely to compete with Ag<sup>+</sup> and thus lower the amount of Ag<sup>+</sup> removed. Therefore, the great Ag<sup>+</sup> adsorption occurring at higher pH could be described to a decrease in competition between H<sup>+</sup> and Ag<sup>+</sup> at the same adsorption site of the adsorbent beads. At pH>6, the



**Fig. 6** Effect of pH on  $Ag^+$  removal at different pH values (initial  $Ag^+$  concentration=100 mg/L, adsorbent dose =4 g/L contact time=30 min and *T*=298 K)

Ag<sup>+</sup> ions begin to hydrolyze and then form insoluble silver hydroxide. At this time, both adsorption and precipitation are effective mechanisms in the removal of Ag<sup>+</sup> ions from aqueous solution [37]. Therefore, the maximum adsorption occurs at around pH 5.0 and it is therefore selected for all adsorption experiments in this study. In order to check the stability of Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>/ ASA in acidic medium, the reaction mixture in pH 5 (optimized pH) was subjected to the elemental analysis by ICP-AEM technology and no Ni, Zn and Fe were detected, which indicated that the spinel structure of Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> was stable.

3.1.3 Effect of adsorbent dosage

The effect of change in the adsorbent amount on the process adsorption of  $Ag^+$  was investigated, with different adsorbent doses in the range of 0.01–0.50 g. The results obtained are shown in Fig. 7. From Fig. 7, it is considered that as the adsorbent dose is enhanced, the removal rate also increases, until it approaches a saturation point, where the enhancement in adsorbent dose does not alter the removal rate. An increase in adsorption rate with adsorbent quantity can be ascribed to the increased surface area and the availability of more adsorption sites. The best removal rate of  $Ag^+$  is about 98.3%, using an adsorbent dosage of 0.20 g in 50 mL of 100 mg/L  $Ag^+$  solution (4 g/L).



**Fig.** 7 Effect of adsorbent dosage on removal efficiency of  $Ag^+$  ions (initial  $Ag^+$  concentration=100 mg/L, pH=5, contact time=30 min and *T*=298 K)

#### 3.1.4 Effect of initial Ag<sup>+</sup> concentration

Batch adsorption experiments were performed at different initial  $Ag^+$  concentrations (50, 100, 200, 300, 500, 700 and 1000 mg/L), while other experimental parameters were constant. Figure 8 shows that adsorption capacity of  $Ag^+$  increases, but the removal efficiency of  $Ag^+$  does not increase too much, indicating that the adsorption of  $Ag^+$  onto  $Ni_{0.5}Zn_{0.5}Fe_2O_4/ASA$  is related to initial  $Ag^+$  concentration. This observation can be described considering the fact that by increasing the

initial  $Ag^+$  concentration, more  $Ag^+$  ions are available, while the amount of active sites on adsorbent is constant, which causes to decrease or remain constant *R*.



**Fig. 8** Effect of initial  $Ag^+$  concentration on removal efficiency of  $Ag^+$  (adsorbent dose=4 g/L, pH=5, contact time=30 min and *T*=298 K)

#### 3.2 Adsorption isotherms

Isotherms study can explain how an adsorbate interacts with adsorbent. The experimental data were corresponded by Langmuir, Freundlich and Dubinin–Radushkevich models as shown in Table 1.

Langmuir isotherm model, which defines a monolayer adsorption, is given in Eq. (3):

$$\frac{1}{q_{\rm e}} = \frac{1}{K_{\rm L} q_{\rm m}} \frac{1}{c_{\rm e}} + \frac{1}{q_{\rm m}}$$
(3)

where  $q_e$  is the amount of Ag<sup>+</sup> adsorbed per unit mass at equilibrium (mg/g);  $q_m$  is the maximum amount of adsorbent that can be adsorbed per unit mass adsorbent (mg/g);  $c_e$  is the concentration of adsorbent (in the solution at equilibrium, mg/L);  $K_L$  is the adsorption equilibrium constant.

A plot of  $1/q_e$  versus  $1/c_e$  gives a straight line, with a slope of  $1/(K_Lq_m)$  and intercept of  $1/q_m$ .

The main characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor  $R_L$  that is given by Eq. (4) [38]:

$$R_{\rm L} = \frac{1}{1 + K_{\rm L}c_0} \tag{4}$$

where  $c_0$  is the highest initial concentration of adsorbate (mg/L), and  $K_L$  (L/mg) is the Langmuir constant. The value of  $R_L$  shows the shape of the isotherm to be either unfavorable ( $R_L$ >1), linear ( $R_L$ =1), favorable ( $0 < R_L < 1$ ), or irreversible ( $R_L$ =0). The  $R_L$  values between 0 and 1 indicate favorable adsorption.

Freundlich isotherm is expressed by Eq. (5). This isotherm model defines a heterogeneous adsorption with different surface energy sites and supposes the change of uptake with exponential distribution of adsorption sites and energies [39-41].

$$\lg q_{\rm e} = \lg K_{\rm F} + 1/n \lg c_{\rm e} \tag{5}$$

where  $c_e \text{ (mg/L)}$  and  $q_e \text{ (mg/g)}$  are the equilibrium concentration of adsorbent in the solution and the amount of adsorbent adsorbed at equilibrium respectively;  $K_F \text{ (mg}^{1-1/n} \cdot L^{1/n} \cdot g^{-1})$  and *n* are the Freundlich constant which indicate the adsorption capacity for the adsorbent and adsorption intensity, respectively.

A plot of lg  $q_e$  versus lg  $c_e$  gives a straight line of slope 1/n and intercept lg  $K_F$ . The value of 1/n mentions the adsorption intensity and the type of isotherm to be favorable (0.1 < 1/n < 0.5) or unfavorable (1/n > 2).

In order to discern between physical and chemical adsorption, the sorption data were analyzed using Dubinin–Radushkevich (D–R) equation, which is given by Eq. (6):

$$\lg q_{\rm e} = \ln q_{\rm m} - \beta \varepsilon^2 \tag{6}$$

where  $\beta$  is a constant related to the mean energy of adsorption (mol<sup>2</sup>/kJ<sup>2</sup>),  $q_{\rm m}$  is the maximum adsorption capacity of metal ions (mg/g),  $\varepsilon$  is the Polanyi potential given by Eq. (7):

$$\varepsilon = RT \ln(1 + 1/c_e) \tag{7}$$

where *R* is the mole gas constant (8.314 J/(mol·K) and *T* is the temperature (K). By plotting  $\ln q_e$  versus  $\varepsilon^2$  with experimental data, a straight line is obtained. From the intercept and slope, the values of  $q_m$  and  $\beta$  are determined. With the value of  $\beta$ , the mean energy *E*, which is the free energy transfer of 1 mol of solute from infinity to the surface of adsorbent, can be obtained by Eq. (8):

$$E = \frac{1}{\sqrt{2\beta}} \tag{8}$$

For E < 8 kJ/mol, the adsorption process might be performed physically, while chemical adsorption when E > 8 kJ/mol [42]. All the parameters are listed in Table 2.

Table 2 Langmuir, Freundlich, D–R isotherm constants for adsorption of  $Ag^+$  ions onto  $Ni_{0.5}Zn_{0.5}Fe_2O_4/ASA$ 

T an annain	$q_{\rm m}/({\rm mg}\cdot{\rm g}^{-1})$	$K_{ m L}$	$R_{ m L}$	$R^2$
Langmuir	243.90	1.46	$6.83 \times 10^{-4}$	0.998
Ess all'st	1/ <i>n</i>		K <sub>F</sub>	$R^2$
Freundlich -	0.50	8	.044	0.988
Dubinin-	$q_{ m m}$ /	β/	<b>p</b> <sup>2</sup>	E/
Radushkevich	$(mg \cdot g^{-1})$	(mol <sup>2</sup> ·kJ	<sup>-2</sup> ) <sup><i>K</i></sup>	$(kJ \cdot mol^{-1})$
(D-R)	139.18	$4 \times 10^{-1}$	-8 0.870	3.540

#### 3.3 Mechanism of adsorption

From Table 2, in which the Langmuir, Freundlich, D-R isotherm constants for the adsorption of  $Ag^+$  are

summarized, it can be derived from  $R^2$  that the Langmuir and Freundlich models matched the experimental data better than D-R model. The values can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate in plane of the adsorbent surface. To confirm the favorability of the adsorption process, the separation factor  $(R_L)$  was determined and given in Table 2. In this study,  $R_{\rm L}$  value of  $6.83 \times 10^{-4}$  shows the favorable adsorption between Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>/ASA and  $Ag^+$ . However, the multilayer adsorption of  $Ag^+$  through the adsorption process may be possible. The Freundlich parameter, 1/n, is related to the adsorption intensity of the adsorbent. When  $0.1 < 1/n \le 0.5$ , the adsorption of the adsorbate is easy; when  $0.5 < 1/n \le 1$ , there is a difficulty with the adsorption; when 1/n > 1, it is quite difficult to adsorb [43,44]. In our study, the value of 1/n (0.50) favorable shows the adsorption of  $Ag^+$ on Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>/ASA. Moreover, from the D-R isotherm constants, it is clear that the adsorption of  $Ag^+$  by Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>/ASA may be explained as physical adsorption process for the value of E is 3.54 kJ.

#### **3.4 Desorption studies**

In metal ion adsorption process, it is significant to easily desorb the adsorbed metal ions under appropriate conditions. In the desorption studies, 0.1 mol/L Na<sub>4</sub>-EDTA was used as desorption agent. The Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>/ASA samples loaded with the maximum amount of Ag<sup>+</sup> ions were placed in desorption medium and the amount of ions desorbed within 1 h measured. Figure 9 shows the data of repeated adsorption/ desorption cycles for Ag<sup>+</sup> ions after 5 cycles. The data show that there is a slight decrease in the adsorption capacity of the Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>/ASA with progressing cycles. Therefore, we can conclude that adsorbent, Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>/ASA, can be used repeatedly without significant loss of its adsorption capacity.



**Fig. 9** Adsorption capacity of  $Ni_{0.5}Zn_{0.5}Fe_2O_4/ASA$  to  $Ag^+$  ions during repeated adsorption/desorption cycles (Experimental conditions: initial concentration of  $Ag^+$  ions=200 mg/L, pH=5.0, temperature=298 K)

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The adsorption capacity is a significant parameter which determines the performance of an adsorbent. Table 3 compares the maximum adsorption capacity of  $Ni_{0.5}Zn_{0.5}Fe_2O_4/ASA$  for  $Ag^+$  adsorption with that of other adsorbents in the literature.

Table 3	Maximum	adsorption	capacity	of	different	adsorbents
for Ag <sup>+</sup>	removal					

Adsorbent	$q_{ m m}/$ (mg·g <sup>-1</sup> )	Saturation time/min	Ref.
Rice husk	1.62	15	[45]
Expanded perlite	8.46	120	[46]
Chitosan	26.88	180	[23]
Clinoptilolite	43.00	45	[47]
Mesoporous silica	46.00	20	[48]
Calcium alginate bead	52.00	240	[49]
Chitosan/bamboo charcoal composite	52.91	150	[23]
Manganese oxide-modified vermiculite	69.20	120	[50]
Valonia tannin resin	97.08	180	[51]
Modified chitosan resins	146.9	20	[52]
Ni <sub>0.5</sub> Zn <sub>0.5</sub> Fe <sub>2</sub> O <sub>4</sub> /ASA	243.90	30	This study

#### **4** Conclusions

 $Ni_{0.5}Zn_{0.5}Fe_2O_4/ASA$  magnetic nanoparticles were used in adsorption of  $Ag^+$  ions from aqueous systems and the maximum  $Ag^+$  adsorption occurred in the pH 5 with maximum adsorption capacity of 243.90 mg/g at 25 °C. The adsorption isotherm fitted the Langmuir and Freundlich models well. The prepared magnetic adsorbent can be well dispersed in the aqueous solution and easily separated from the solution with the aid of an external magnet after adsorption. The process of water treatment described here is clean and safe using the magnetic nanoparticles. Thus, this adsorbent was found to be useful and valuable for controlling water pollution due to  $Ag^+$  ions.

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### 采用负载 Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> 磁性纳米粒子 芦荟壳灰从水溶液中快速高效去除 Ag(I)

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**摘 要:** 采用负载 Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> 磁性纳米粒子芦荟壳灰从水溶液中去除 Ag(I)。采用 XRD、SEM、BET 等温线、 振荡试样磁力计(VSM)和傅里叶变换红外光谱(FT-IR)表征该吸附剂。采用该吸附剂在不同 pH 值(2~7)、吸附剂量 (0.01~0.5 g)、Ag<sup>+</sup>浓度(50, 100, 200, 300, 500, 700 和 1000 mg/L)下测定 Ag(I)的吸光度。在最佳条件(30 min, pH=5) 下,得到最高的 Ag<sup>+</sup>去除率。在 50 mL 100 mg/L Ag<sup>+</sup>溶液中,最佳吸附剂量是 0.20 g,去除率为 98.3%。基于 Langmuir 等温线,得到最大单层饱和吸附量为 243.90 mg/g。表征结果表明,吸附剂的比表面积和孔体积分别为 814.23 m<sup>2</sup>/g 和 0.726 cm<sup>3</sup>/g。实验数据与 Langmuir 和 Freundlich 等温线模型吻合。合成的吸附剂对水溶液中 Ag(I) 吸附具有理想的表面积和吸附容量。

关键词: 吸附; Ag<sup>+</sup>离子; Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>; 芦荟

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