I.A.U. Karaj Branch

Journal of Applied Chemical Research, 10, 2, 39-49 (2016)

Journal of Applied Chemical Research
www.jacr.kiau.ac.ir

Separation and Recovery of Platinum by Magnetic Core-shell Nanostructures Modified with N-(2-aminoethyl)-3-aminopropyltrimethoxysilane

Mansoor Anbia*, Ruholla Mehrizi

Research Laboratory of Nanoporous Materials, Faculty of Chemistry, Iran University of Science and Technology, Tehran

(Received 20 Jan. 2016; Final version received 14 Mar. 2016)

Abstract

In this paper, $Fe_3O_4@SiO_2$ core/shell magnetic nanostructure has been synthesized and modified by N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPTMS). $Fe_3O_4@SiO_2$ was used as a novel adsorbent for separation of hexachloroplatinic acid. X-ray diffraction (XRD), scanning electron microscopy (SEM), and FT-IR technique were used to characterize morphologies and surface texturing of these adsorbents. The effective factors on adsorption, such as pH, contact time; salt effect and temperature were studied systematically. The optimal conditions of Platinum adsorption were obtained at temperature of about 25°C, pH about 2.5 and the equilibrium time of 30-40 minutes. The maximum adsorption capacity (q_{max}) in the optimal conditions was equal to 74 mg/g. The magnetic separation of the absorbent was achieved by a magnet and finally the absorbent was compared with other absorbents. Inductive coupled plasma optical emission spectrometer (ICP-OES) was used for determination of metal ion concentrations in the aqueous solution.

***Keywords**: Platinum, adsorption, Magnetic core-shell, nanostructure, Magnetic separation.*

Introduction

For leaching and recovery of platinum in faulty Catalyst, aqua regia is added. In this reaction, platinum metal will be converted to hexachloro palatinate anion [1]. Thus, the use of a technique for separation of this material is necessary. Several different types of methods, such as chemical precipitation, solvent extraction, nanofiltration, and adsorption, have been used for the removal of metal ions. Among of

***Corresponding author:** Dr. Mansoor Anbia, Research Laboratory of Nanoporous Materials, Faculty of Chemistry, Iran University of Science and Technology, Tehran, Iran. E-mail:anbia@iust.ac.ir. Tel: +98-21-77240516, Fax: +98-21-77491204.*

these methods, adsorption [2] has increasingly received much attention because of its high efficiency, simple operation, and environmental friendliness. herein, a variety of adsorbents including activated carbon [3], modified silica gel [4], chitosan microspheres [5] and Fe_3O_4 nanoparticles [6] have been reported as materials for the adsorption of metal ions.

Easy separation from treated water is the other necessity of a promising adsorbent. Conventional methods such as precipitation, centrifugation, filtration and chromatography are not only usually difficult and uneconomical, but also are expensive and out of reach. Therefore, convenient and effective separation methods are needed. Magnetic materials can be easily and rapidly separate from aqueous solutions under an external magnetic field. Simplicity, high efficiency and sensitivity as well as low costs are some advantages of these materials. Therefore, introducing Fe_3O_4, which features superparamagnetism into the prepared adsorbent is a good way to resolve the problem of separation[7]. Time progression is an important parameter determining the cost of the process. Furthermore, magnetic separation method is also beneficial with regard to the environment because it does not result in the production of contaminants such as flocculants [8]. This makes magnetic nanoparticles as excellent candidate for combining metal binding and selective adsorption properties with ease of phase separation[9].

The magnetite nanoparticles are prepared by the conventional precipitation method [10] or solvothermal reaction[11]. Fe_3O_4 is not stable under acidic conditions and it is prone to aggregate and show poor dispersion in water. It is also difficult to graft the surface of Fe3O4 with organic materials since there are few hydroxyl groups on the surface of Fe_3O_4 [12]. Therefore, modification and surface coating for Fe_3O_4 is necessary. Many kinds of materials have been discovered in recent years for use as the coating, including noble metals, metal oxides and inorganic silica. Among these coating materials, silica is very promising since the dense silica shell may prevent Fe_3O_4 cores from chemical contact with corrosive liquid media and, most importantly, the surface chemistry of a silica shell is compatible with various chemicals and molecules for bio-conjugations. SiO_2 is nontoxic and stable under acidic conditions and also inert to redox reactions, as compared with the organic coating materials, and hence it is an ideal shell composite to protect the inner magnetite core[10]. By taking these advantages of silica, it has been proved experimentally that the silica surface works well with various coupling. It is stable and easily dispersible. Two approaches are used for coating silica onto Fe_3O_4 nanoparticles include the alkaline hydrolysis of Tetraethyl orthosilicate (TEOS) [13] and acidic hydrolysis of sodium silicate . The SiO_2 coating shell has an abundance of

surface hydroxyl groups, which offers ease of succedent functionalization of magnetite nanoparticles [10]. The shell thickness of silica shell can be tuned by adjusting the amount of silica source and reaction process[11]. Three experimental parameters influence on silica shell thickness including (1) the reaction time; (2) the ratio of sodium silicate to Fe_3O_4 NPs; and (3) temperature. The functional groups on the SiO_2 shell play an important role in determining the effectiveness, capacity, selectivity, and reusability of these adsorbents[8]. these nitrogen-containing soft base compounds have high selectivity towards precious metals, which are typically soft acids [14].

In this work, Fe_3O_4@SiO_2 core/shell magnetic nanostructure has been synthesized and modified by AEAPTMS for separation of hexachloroplatinic acid. The textural properties of the material was studied by XRD analysis, SEM photograph and FT-IR technique. The adsorption of Platinum and effective factors on adsorption, such as pH, contact time, salt effect and temperature were studied systematically. The magnetic separation of the absorbent is achieved by a magnet and finally the absorbent is compared with other absorbents.

Experimental

Apparatus

The X-ray powder diffraction patterns were recorded on a Philips 1830 diffractometer using Cu -Kα radiation. For SEM the PHILIPS XL30 was used to analyze product morphology. The FT-IR spectra were measured with KBr pellet using a DIGILABFTS 7000 instrument within the wavelength range of 400–4000 cm-1. Inductive coupled plasma optical emission spectrometer (ICP-OES) was used for determination of metal ion concentrations in the aqueous solution.

Reagents

All the reagents used were of analytical grade. Iron(II) chloride tetrahydrate ($FeCl_2$•$4H_2O$), iron(III) chloride ($FeCl_3$), NH_4OH, hydrochloric acid (HCl, 37%), nitric acid (65%), Sodium silicate, N-(2-Aminoethyl)-3-(trimethoxysilyl)propylamine (AEAPTMS), Sodium chloride (99.5%), Toluene (>99%), Acetone (99.5%), hexachloroplatinic acid hexahydrate ($H_2(PtCl_6)6H_2O$), were from E. Merck (Darmstadt, Germany).

Synthesis of Fe_3O_4 nanoparticles

$FeCl_2.4H_2O$ (4.9 g) were dissolved in 177 ml deionized water in the flask under ultrasonication at 65 0C for 20 min. then, $FeCl_3.6H_2O$ (12 g) added to the flask under nitrogen atmosphere. After that, 80mL of 28% aqueous ammonia was added into the flask with stirring at 80 0C for 40 min and then 100 ml deionized water added to the flask. The produced magnetic NPs were washed by deionized water and ethanol for several time, and then dried at 50 ^oC under vacuum.

Synthesis of Fe_3O_4@SiO_2 core/shell

Synthesized Fe_3O_4 (2 g) were added to 400 ml deionized water and sonicated for 30 min. The magnetic suspension prepared was heated to 80 0C under vigorous stirring. Then, sodium silicate solution (1.0 M) was added to the Fe_3O_4 suspension. The pH of the suspension was adjusted to 6.0 using HCl solution (2 mol/L), and the mixture was stirred at 80 ^oC for 3 h. The silica-coated Fe_3O_4 nanoparticles were washed with deionized water, followed by drying at 50 ^oC under vacuum for 24 h.

Synthesis of Fe_3O_4@SiO_2 core/shell modified by AEAPTMS

Fe_3O_4@SiO_2 (1.76 g) was dispersed in 50 mL of dry toluene and sonicated for 30 min. Then 4 mL of AEAPTMS was added to above solution. The mixture was then refluxed for 14 h under nitrogen flow and at the oil bath temperature of 110 ^oC. The solid product was washed with ethanol to remove excess amounts of amine and filtrated, then dried under vacuum at 500 ^oC. Figure 1 shows the Synthesis route of Fe_3O_4@SiO_2-AEAPTMS.

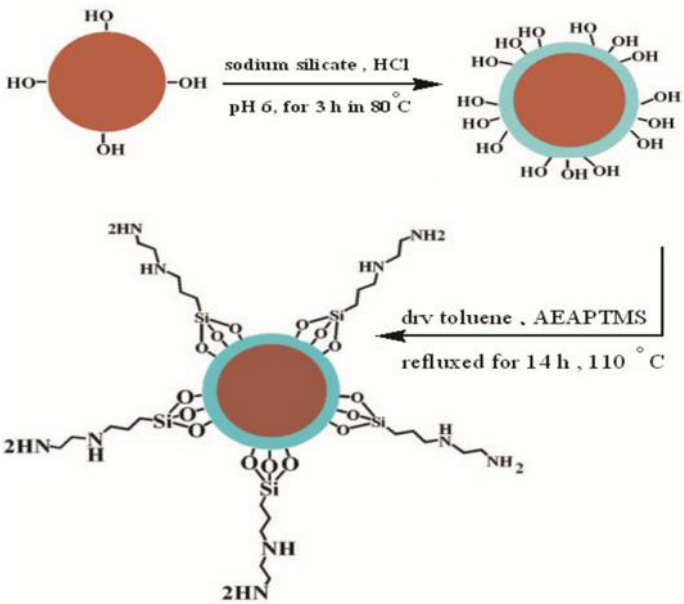

Figure1. the Synthesis route of Fe_3O_4@SiO_2-AEAPTMS.

Results and discussion

Characterization of the Fe_3O_4

SEM micrographs of spherical Fe3O4 NPs are shown in figure 2.

XRD pattern of Fe_3O_4 is shown in figure 3, and illustrates that this model has similarities very well with the standard pattern of magnetic Fe_3O_4. Thus, it is suitable for magnetic separation. The average crystal size of the Fe_3O_4 cores calculated by Scherrer's formula [15] that is about 17 nm.

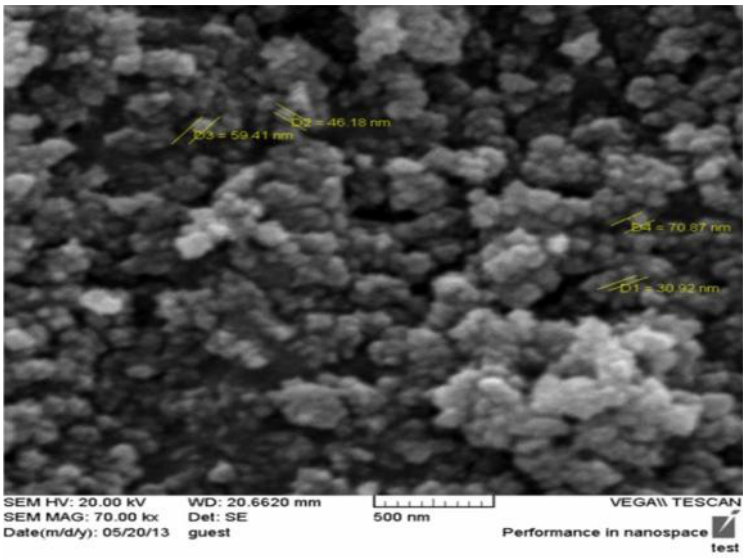

Figure 2. SEM image of Fe_3O_4.

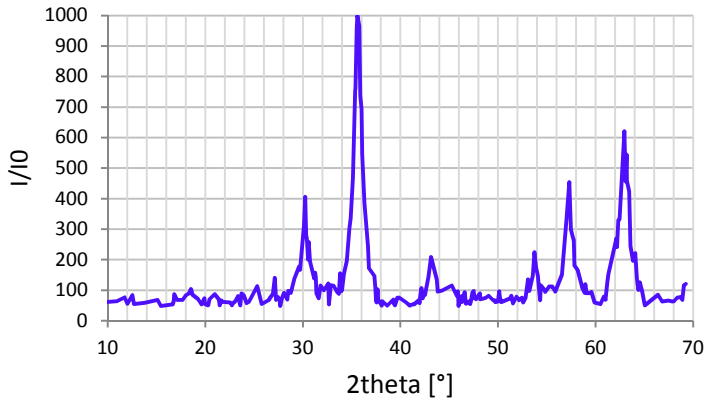

Figure 3. XRD pattern of Fe_3O_4.

Figure 4 shows the FT-IR spectra of Fe3O4 particles and magnetic Fe_3O_4@SiO_2 composite particles and Fe_3O_4@SiO_2 core/shell modified by AEAPTMS. The weak and broad band centered around 3420 cm^{-1} and 1622 cm^{-1} are, respectively, assigned to the O-H stretching and deforming vibrations of adsorbed water. The peak at 580cm^{-1} is ascribed to Fe-O stretching vibration. The characteristic absorption peaks of SiO_2 at 1100 cm^{-1}, 800 cm^{-1}, 950 cm^{-1} and 468 cm^{-1}, which are attributed to asymmetric and symmetric stretching vibrations of Si-O-Si, stretching vibration of Si-O-H and bending vibration of Si-O-Si respectively. Peaks at 600 cm^{-1}, 3420 cm^{-1} and 1100 cm^{-1} indicated that magnetic Fe_3O_4 is covered by SiO_2 layer. Reduction of transition in 468, 800, 950 and 1100 cm^{-1} are assigned to the SiO_2.

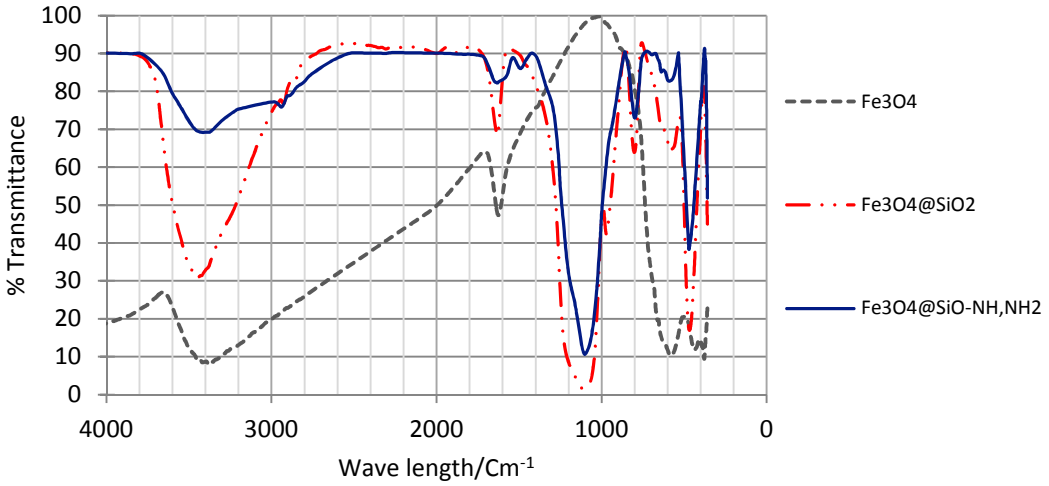

Figure 4. FT-IR spectra of $Fe_3O_4$and Fe_3O_4@SiO_2 and Fe_3O_4@SiO_2 core/shell modified by AEAPTMS.

The effect of pH on adsorption of hexachloroplatinate anion

pH may affect both aqueous chemistry and surface binding sites of the adsorbent [16]. A negative polarization of its surface occurs at pH higher than 1 (negative zeta potential) but becomes significant only at pH above 7. In other words, silica may only adsorb cations, and this phenomena becomes important only at pH above 7 [17]. Therefore, silica-coated iron oxide nanoparticles cannot absorb the hexachloroplatinate anion. In this study, silica shell was optimized by amino group and so at suitable pH the protonated amines are able to absorb the hexachloroplatinate anion. The effect of pH on the adsorption is shown in figure 5. Positively charged surfaces (at pH<PZC) are capable of adsorbing anions, and negatively charged surfaces (pH >PZC) are capable of adsorbing cations [17].

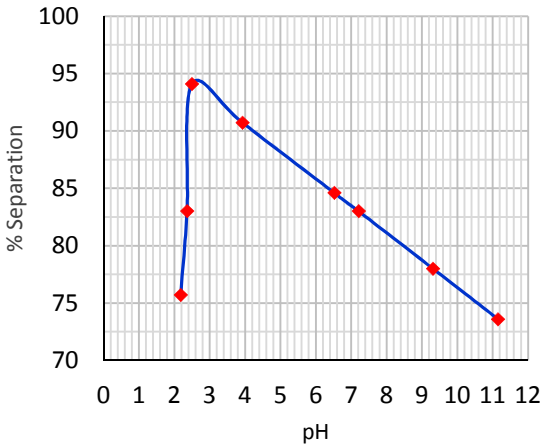

Figure 5. Effect of pH on adsorption of hexachloroplatinate anion.

The curve indicates that maximum sorption value for Pt (IV) onto magnetic Fe_3O_4@ SiO_2-NH,NH_2 was about 74 mg/g, when the initial concentration of Pt (IV) was 141 mg/L. According to the experimental results pH optimum for adsorption was 2.5 where most of amino groups were protonated, which were favorable for the electrostatic attraction of hexachloroplatinate anion. Therefore, pH 2.5 was selected for the further sorption experiments. Mechanism of metal-chloro complex adsorption on adsorbent (the anion-exchange reactions) is shown in Scheme 1.

$$R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH_2 + 2HCl \rightarrow$$
$$[R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2^+\text{-}CH_2\text{-}\ CH_2\text{-}NH_3^+].2Cl^-$$

$$[R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2^+\text{-}CH_2\text{-}\ CH_2\text{-}NH_3^+].2Cl^- + PtCl_6^{2-} \rightarrow$$
$$[R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2^+\text{-}CH_2\text{-}\ CH_2\text{-}NH_3^+]PtCl_6^{2-} + 2Cl^-$$

Scheme 1. Adsorption Mechanism.

By changing the pH, polarization of adsorbent surface and thermodynamic parameters will be change. Thus electrostatic adsorption of complex will be controlled. Therefore, at acidic pH the proposed mechanism is of anion exchange. Two chloride away and hexachloroplatinate anion will be attracting to polarized adsorbent functional groups. At higher pH, mechanism of adsorption is Lewis acid-base.

The equilibrium adsorbed concentration, qe, was calculated according to the equation1:

$$q_e = \frac{(C_0 - C_e)V}{M} \qquad (1)$$

Where C_o (mmol/L) is the initial concentration of metal ion, C_e (mmol/L) is the equilibrium concentration in solution, V (L) is the total volume of solution, and M (g) is the sorbent mass. Sorption (%) of Pt (IV) from solution was calculated according to the equation 2:

$$\text{Sorption (\%)} = \frac{C_0 - C_e}{C_0} * 100 \qquad (2)$$

For adsorption study, 0.02 g absorbent was added to 9 ml of hexachloroplatinate solution in polyethylene tubes and the tube was shaken in 800 osc / min.

The effect of temperature on adsorption of hexachloroplatinate anion

For better adsorption, absorbent was added to sufficient amount of hexachloroplatinate acid. Then precipitated by centrifugation and added to distilled water and shaken. The temperature of solution increases to a specified value and gives enough time to balance out. After 30 minutes, some of the solution was removed

and centrifuged and remained amount of platinum was measured. According to van Hoff equation in chemical thermodynamics, by changing the temperature, the equilibrium constant of the reaction and desorption will be changed. The decrease of absorption at high temperature indicates that this adsorption is exothermic. The increase in temperature favors for desorption but does not favor adsorption (figure 6).

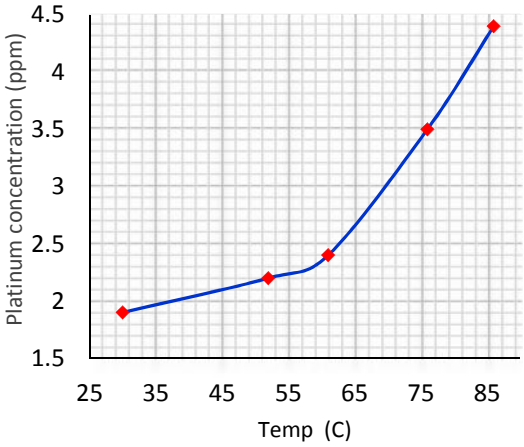

Figure 6. Effect of temperature on desorption of hexachloroplatinate anion.

The effect of contact time on adsorption of hexachloroplatinate anion

The effect of contact time on the adsorption of Pt (IV) is shown in figure 7. The results demonstrate that by increasing contact time, the adsorption will be increased and equilibrium time as attained at around 40 min. This figure reveals that 80% adsorption has occurred in 5 min.

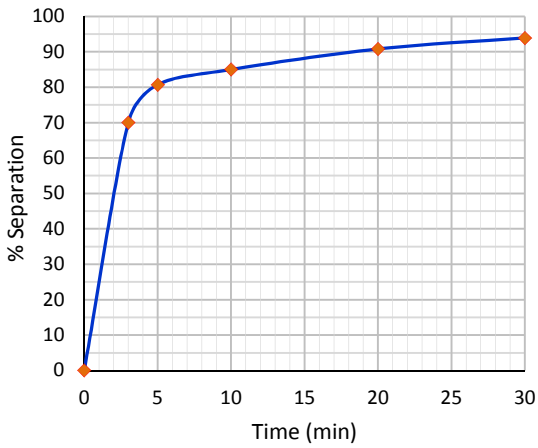

Figure 7. Effect of contact time on separation by Fe_3O_4@SiO_2 core/shell modified by AEAPTMS (pH:2.5, concentration of hexachloroplatinic acid: 141 mg L^{-1}).

The effect of supporting electrolyte concentration on adsorption of hexachloroplatinate anion

One of the major pollutants wastewaters has been identified as sodium chloride. Figure 8 exhibits the effect of sodium chloride concentration on the adsorption of hexachloroplatinate anion by this adsorbent. This figure shows that by increasing Cl− concentration the separation decreased. The effect of background electrolyte on hexachloroplatinate anion adsorption by Fe_3O_4@SiO_2–NH&NH_2 was studied by dispersing 20 mg of adsorbents in 9 ml of NaCl solution (0–10 %) containing 141 ppm Pt(IV) , pH 2.5, at room temperature and contact time 30 min.

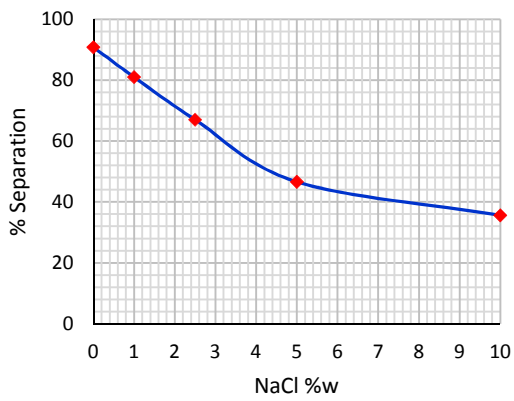

Figure 8. Effect of chloride ion concentration on the amounts of Pt(IV) adsorbed. (pH:2.5, concentration of hexachloroplatinic acid: 141 mgL^{-1} ,contact time: 30 min)

Reduced absorption due to increased ionic strength may be obtained for the following reasons:

1) By increasing the chloride anions concentration, the active sites on the adsorbent will be occupied by the chloride anions.

2) By increasing the chloride anions concentration, adsorption equilibrium of chloride anion is shifted towards consumption of chloride. Therefore concentration of hexachloro platinate anion will increase.

3) By enhancement of chloride anions concentration, the ionic strength solution of anions will increase and activity of hexachloro platinate will decrease. Thus reducing the possibilities of interaction between the adsorbent and adsorbed will altered.

Magnetic separation

Magnetic materials can be easily and rapidly separated from aqueous solutions under an external magnetic field. Fig 9 shows the magnetic separation of dispersed NP using an external magnetic field.

a) b) c) d) e) f)

Figure 9. Digital photograph of the solution (a) dispersed magnetic Fe_3O_4@SiO_2-AEAPTMS particles and magnetic separation (b) using an external magnetic field after 0 min (c) 2 min (d) 3 min (e) 10 min (f)30 min.

Comparison with other adsorbents

Maximum adsorption capacity (q_{max}) and equilibrium time are two important factors for comparison with other adsorbents.

Table 1.The adsorption capacity and equilibrium time of several various adsorbents.

Adsorbent	q_{max} (mg/g)	equilibrium time	References
Fe_3O_4@SiO_2 core/shell modified by AEAPTMS	74	40 min	Present study
Cross linked chitosan resin modified with l-lysine	129.26	120 min	[4]
Fe_3O_4 nanoparticles	13.27	<20 min	[6]
Activated carbon	1.43	3 h	[3]
Magnetic chitosan nanoparticles modified with ethylenediamine	171	< 1 h	[18]
Glycine-modified chitosan	122.47	120 min	[19]

Conclusion

Fe_3O_4@SiO_2core/shellmodifiedbyAEAPTMS have been synthesized for adsorption of hexachloro platinate anion. The prepared magnetic adsorbents can be well dispersed in aqueous solution and easily separated from the solution in 30 min. By increasing the magnetic strength of the magnet, separation speed can be increased. The adsorption capacity in the studied work is 74 mg/g. By acidification and heating, desorption of adsorbed species is possible.

This amino functionalized magnetic silica is an adsorbent for adsorption of hexachloro platinate anion. This adsorption was exothermic attraction. The results have demonstrated that the adsorption process is dependent on pH, temperature, contact time,

background electrolyte.

References

[1] M. Baghalha, H. Khosravian Gh, H.R. Mortaheb, *Hydrometallurgy*., 95, 247 (2009).

[2] M. Anbia, Z. Ghassemian, *Chem. Eng. Res. Des.,* 89, 2770 (2011).

[3] S. Aktas, M.H. Morcali, *Trans. Nonferrous Met. Soc. China*., 21, 2554 (2011).

[4] M. Ghoul, M. Bacquet, M. Morcellet, *Water Res*., 37, 729 (2003).

[5] L. Zhou, J. Liu, Z. Liu, *J. Hazard. Mater.,* 172, 439 (2009).

[6] A. Uheida, M. Iglesias, C. Fontàs, M. Hidalgo, V. Salvadó, Y. Zhang, M. Muhammed, *J. Colloid Interface Sci.,* 301, 402 (2006).

[7] G. Li, Z. Zhao, J. Liu, G. Jiang, *J. Hazard. Mater.,* 192, 277 (2011).

[8] Y. Lin, H. Chen, K. Lin, B. Chen, C. Chiou, *J Environ Sci*, 23, 44(2011).

[9] A. Uheida, G. Salazar-Alvarez, E. Björkman, Z. Yu, M. Muhammed, *J. Colloid Interface Sci.*, 298, 501 (2006).

[10] J. Wang, S. Zheng, Y. Shao, J. Liu, Z. Xu, D. Zhu, *J. Colloid Interface Sci*., 349, 293 (2010).

[11] H. Tian, J. Li, Q. Shen, H. Wang, Z. Hao, L. Zou, Q. Hu, *J. Hazard. Mater.*, 171, 459 (2009).

[12] R.-Y. Hong, J.-H. Li, S.-Z. Zhang, H.-Z. Li, Y. Zheng, J.-m. Ding, D.-G. Wei, *Appl. Surf. Sci*., 255, 3485 (2009).

[13] W. Stöber, A. Fink, E. Bohn, *J. Colloid Interface Sci.*, 26, 62 (1968).

[14] R. G.pearson, *J. Am. Chem. Soc.*, 85, 3533 (1963).

[15] J.I. Langford, A.J.C. Wilson, *J. Appl. Crystallogr*., 11, 102 (1978).

[16] L. Ai, H. Huang, Z. Chen, X. Wei, J. Jiang, *Chem. Eng. J.,* 156, 243 (2010).

[17] J.P. Brunelle, Preparation of Catalysts by Adsorption of Metal Complexes on Mineral Oxides, *Stud. Sur. Sci. Catal.,* 3,211 (1979).

[18] L. Zhou, J. Xu, X. Liang, Z. Liu, *J. Hazard. Mater.*, 182, 518 (2010).

[19] A. Ramesh, H. Hasegawa, W. Sugimoto, T. Maki, K. Ueda, *Bioresource Technol.,* 99, 3801 (2008).