Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Dual application of facial synthesized Fe_3O_4 nanoparticles: fast reduction of nitro compound and preparing of magnetic polyphenylthiourea nanocomposite for efficient adsorption of lead ions

Mostafa Hossein Beyki, Farzaneh Shemirani*

School of Chemistry, University College of Science, University of Tehran, Tehran, Iran.

P.O. Box 14155-6455

E-mail: Shemirani_ Farzaneh@yahoo.com Shemiran@khayam.ut.ac.ir

Fax: +98 2166405141; Tel: +98 21 61112481

Fig. S_1. The image of prepared organic compound.

Fig. S_2. Amount of iron released from PNC structure after 5 cycle (a) and the FT – IR spectra of PNC after 5 cycle of sorption and desorption (b).

1.1. Preparation of nitro aniline. In the first step acetanilide was synthesized with following procedure: [1] about 10 ml of aniline placed in 50 ml round bottom flask and 15 ml of glacial acetic acid and 0.3 g of zinc powder was added to it. The flask was connected to a condenser that will be employed only as an air condense and water do not passed through it. The mixture was heated such a rate that the temperature of vapor on top of the condenser was reached to 100-105 after 2h then, the mixture was purred in a 100 ml cooled water and the crude product was washed with water to be free of acid. In order to preparing pure acetanilide, the product was added to 100 ml of water and dissolved completely by heating on hot plate. Then 5 g of activated carbon was added to it and filtered from hot funnel. The clear solution was placed in room temperature for 2 h and the obtained crystals were collected with filter paper and dried for 24 h in room temperature.

To preparing 4-nitroaceanilide, 5 ml of glacial acetic acid and 10 ml of concentrated H_2SO_4 separately have been added to 5.0 g of acetanilide then the mixture was placed in ice bath. A mixture of 2.2 ml of concentrated HNO_3 and 1.4 ml of H_2SO_4 was placed in ice bath till its temperature reached below 5°C then was added gradually to acetanilide solution while the temperature remained below 10 °C. After adding all mixed acid to acetanilide, about 100 ml of cooled water added to it and the obtained white solid placed in room temperature for 30 min, filtered with filter paper and washed several time with distilled water until the yellow 2-nitroacetanilide have been removed from the 4-nitroacetanilide. The prepared white solid was dried in room temperature. In subsequent step; 3.0 g of 4-nitroacetanilide was refluxed in 25 mL of H_2SO_4 solution(70%) for 20 min then diluted with 50 mL of distilled water. To precipitate the 4- nitro aniline, concentrated ammonia was added to nitroacetanilide solution and nitro aniline was collected as yellow crystals with filter paper (melting point 147 – 151°C). The image for prepared compounds is depicted in figure S_1.

Fig.S_1

1.2. Effect of time and sample volume. The effect of the contact time on the extraction efficiency was investigated by applying the adsorption procedure for 50 mL of lead solution (10 mg L^{-1}) from 1 to 10 min. The value of Qe increased rapidly within the first 2 min because of the availability of large number of adsorption sites and then which the sites are gradually filled up the kinetics will be more dependent on the rate at which the analyte is transported from the liquid phase to the adsorption sites. The increase in Qe was not significant after 3 min hence, the time of 3 min was selected for further works.

In order to investigate the applicability of the presented method to enrichment of trace level of lead ions from high volume the adsorption method was applied for different sample solution from 50 – 500 mL containing 5.0 μg of target ions. The results indicated that the recovery was quantative from 400 mL of sample solution and after elution with 5.0 mL of HNO_3 solution the preconcentration factor of 80 was obtained.

1.3. Desorption and reusability. To examine the reusability of PNC for adsorption of trace level of lead ions different concentrations of HNO_3 solution (0.1, 0.2. 0.3, 0.5 mol L^{-1}) were tested. The results indicated that with 5 mL of 0.3 mol L^{-1} of HNO_3 solution, the recovery was more than 98%. Hence, the described situation were used as the optimum conditions for lead desorption. Furthermore the PNC was subjected to several loadings with the sample solution and subsequent elution. It was found that the recovery remained constant (95–98%) after 5 cycles of sorption and desorption. Moreover, the stability of magnetic PNC in acidic media was investigated by using FAAS and FT-IR technique. Amount of dissolved iron in each cycle as a result of elution was determined with FAAS and the results (S_2a) indicate that about 4% of iron was dissolved after 5 cycle of desorption. The IR spectrum (S_2b) shows that the structure of prepared composite was not changed after 5 cycle and indicate that the PNC has good stability in acidic medium.

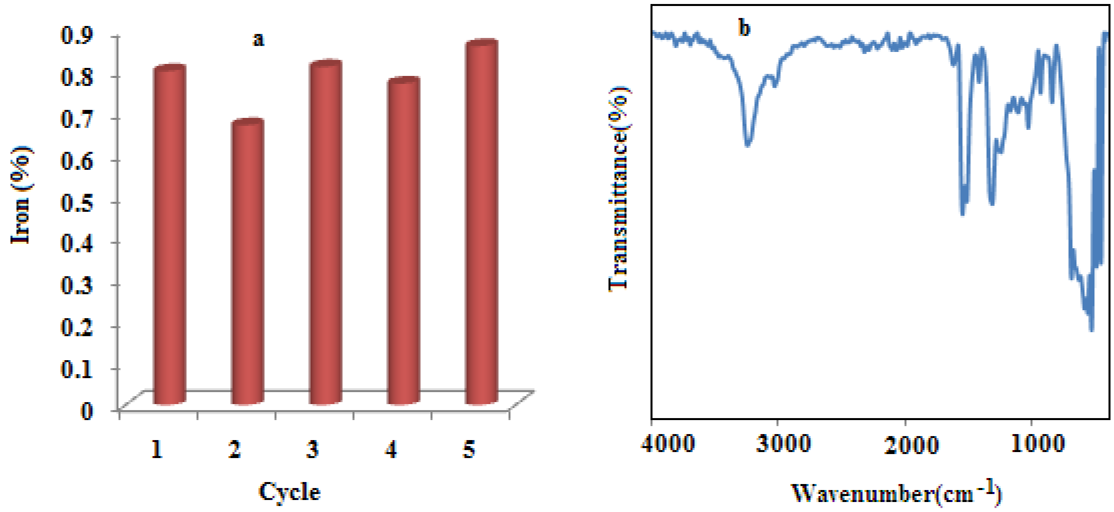

Fig.S_2

1.4. Analytical features. Under optimized conditions, calibration curves were constructed for the determination of lead according to the preconcentration procedure. The linearity in the final solution was maintained between 2.0 and 100 mgL^{-1} with a correlation factor of 0.998 ($A=0.562C–0.006$). The procedure was repeated six times and the relative standard deviation in the determination of 0.1 mg L^{-1} of Pb(II) ion was found to be 2.5%. The limit of detection (LOD) was 0.22 μgL^{-1} and was defined as $3S_b/m$, where S_b is the standard deviation of eight replicates of blank signals and m is the slope of the calibration curve after preconcentration.

(1) Vogel, A. I., D. Sc. (Lond.), D.I.C., F.R.I.C . A Text Book of Practical Organic Chemistry Including Qualitative Organic Analysis. Third Edition, London, **1956**, pp, 577 - 581.