Open Journal of Polymer Chemistry, 2016, 6, 9-14
Published Online May 2016 in SciRes. http://www.scirp.org/journal/ojpchem
http://dx.doi.org/10.4236/ojpchem.2016.62002

The Phosphochlorinated Polymeric Sorbents for Sorption of Gold (III)

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Received 31 July 2015; accepted 17 July 2016; published 20 July 2016

Abstract

This study evaluated the simple methods to improve the sorptional capability of polymeric sorbent to gold (III) ions. The polymeric sorbents have been synthesized by a chemical modification of dithizone phosphorchlorinated PB. The structure and composition of functional polymers are studied by IR spectroscopy, X-ray fluorescence analysis, the diffusion of optical spectroscopy, scanning electron microscopy, thermogravimetric and elemental analysis. It found that the obtained sorbents had porous crosslinked structure and did not dissolve in any organic solvents, solutions of inorganic acids and alkalines. The sorption properties of the syntesized polymer sorbents onto gold (III) ion in aqueous solutions have been studied. It is found that the adsorption effect of gold makes 85% - 90% and the equilibrium sorption capacity of polymer sorbent is 137 mg/g in acidic media. In order to improve sorption efficiency of sorbents to gold ions, the non-covalent immobilization of organic sulfur containing compound to the polymer matrix was carried out. The gold embedded polymer matrix was characterized by SEM, EDX, XRD and visible absorption spectroscopy. The obtained results indicated that the polymeric sorbent contained metallic form of zero-valent gold. It was found that the average particle size of elemental gold crystals was 28.31 nm.

Keywords

Sorption, Gold, Phosphochlorinated Polymer

1. Introduction

Nanogold composite materials have large applications such as nanoelectronic devices, catalyst, sensors, optical, anti corrosion materials and etc. [1]-[6]. Determination of gold ions in environmental and geological samples requires very often preconcentration and separation by polymer sorbents due to the high concentration of inter-

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How to cite this paper: Azizov, A.A., Yaqubova, U.I. and Aliyev, M.I. (2016) The Phosphochlorinated Polymeric Sorbents for Sorption of Gold (III). *Open Journal of Polymer Chemistry*, **6**, 9-14. http://dx.doi.org/10.4236/ojpchem.2016.62002

fering matrix components and the low content of this metal. Solid phase extraction technique offers for this purpose high enrichment factor, rapid phase separation and the ability of combination with different detection techniques [7] [8]. It is very clear that physicochemical properties of polymers (e.g. sensing and separation) are enhanced by anchored nanoparticles, while polymers provide excellent platforms for dispersing nanoparticles for e.g. high catalytic performances [9]-[11]. For nanogold produce is used chemical, physical, biochemical methods [12]-[14], gold nanoparticles have been prepared chemically through the reduction of hydrogen tetrachloroaurate using suitable reducing agents in the presence of stabilizers. Several works have been published regarding the successful application of polymers with metal binding sites as stabilizers in the preparation of gold nanoparticles with a controlled size and narrow size distribution [15] [16]. The one of the main condition of the matrix selection is to be financially affordable. Here we report the uptake of gold ions from the aqua solutions using porous sorbent immobilized sulfur containing organic reagent which is sensitive toward gold. In the result of sorptional proses, the gold nanoparticles formed in the sorbent phase. The synthesized polymer sorbent has a porous matrix which can used to form nanogold particles by sorption-reducing method.

2. Methods

The polymeric sorbent is produced on the basis of phosphochlorinated synthetic butadiene rubber SBR, as a result of the modification thereof by an oxidative chlorophosphorylation reaction method as reported [17]. Derived product has crosslinked structure, deep brown color, undissolved in acid, alkali and other organic solvents. The spherical of polymer granules have a porous structure with an average bead diameter 250 - 400 microns, which can sorb chemical compounds by physical adsorption such as Van der Waals forces, dipolar bonds.

The stock gold solution was prepared by dissolving 1 g metallic gold in aqua regia (($HCl + HNO_3$) (3:1)), following dilution with deonizined water to 1000 ml. Chloroauratic acid solutions in $[AuCl_4]^-$ ion form with an average concentration of 100 - 500 mq/l were prepared by diluting from the stock solution in 1 g/l concentration. Au (III) concentration after uptake of gold ions using polymer sorbent in the solution was determined by Atomic absorption spectroscopy, at a wavelength of 242.4 nm.

Despite the fact that this sorbent is used for uptake of heavy metal ions due to having an phosphate acid groups, can make a property to sorb gold ions from aqous water. This concern has been achieved for non covalent immobilization as a result of treating of polymer sorbent with organic reagent which can interreact with gold ions. Thiourea is used as an immobilizated reagent. The immobilization was attempted in a batch process by mixing dried polymer cubes with thiourea solution heating up to 80˚C. The thiourea immobilized polymer cubes was then filtered, and dried at 50˚C under the vacuum to constant weight. The sorption of gold ions from an aqueous gold (III) solution was attempted in a batch process for 1 h at room temperature. After sorption process polymer is dried for 24 h at 50˚C. Residual amount of gold ions in solution were analyzed by Atomic absorption spectroscopy. SEM, EDX, XRD analyses are used for gold forming investigation in the polymer phase.

3. Results and Discussions

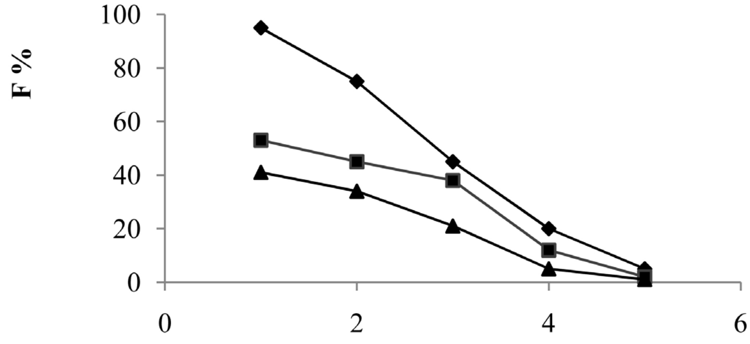
The adsorption efficiency was studied for varying the initial concentration, acidity, amount of sorbent, distribution coefficient at 22˚C for an initial period of 60 min. The effective adsorption efficiency was obtained at 2 M HCl solution (**Figure 1(a)**). Increasing the concentration of the gold ions in the solution the adsorption efficiency increases which is describe as L type sorption isotherm (**Figure 1(b)**)

This behavior is most likely attributed to an instability of the produced complex species formed between gold (III) ion and the reagent immobilized polymer of the produced complexion assoside of $[AuCl_4]^-$ with the sorbent site of the thiourea noncovalent immobilized polymer. No significant increase in the efficiency was obtained with use of metal solution concentration beyond 0.8 mmol/l. The sorption efficiency stabilized after determined concentration. It can be attributed to the saturation of active sites on the polymer matrix. The value of maximal sorption capacity is calculated as a 0.647 mmol/g^{-1}.

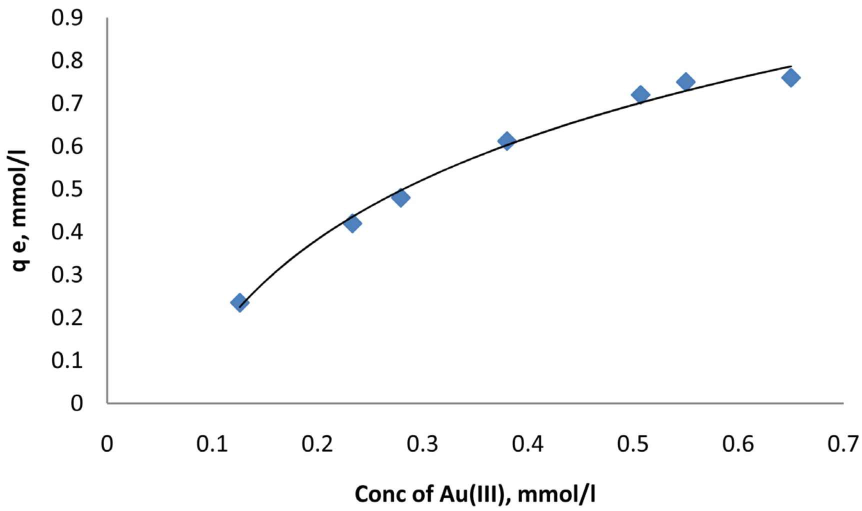
Adsorption efficiency decreases with increase acid concentration. It can be attributed to a competition of chlorine ions. The distribution coefficient decreases with the increase concentration of gold ions from aqueous solution which can be attributed to the free movement limitation due to the metal ions overage in aqueous media (**Figure 1(c)**).

The XRD pattern for the polymer sorbent after uptake of gold (III) ions from aqueous media is shown in **Figure 2**.

From the XRD pattern we get the d spacing values which are calculated from the observed reflections



(a)



(b)

Initialconc. of Au (III) ion	25	45	55	75	100	150
Eq.conc. of Au(III) ion	3.11	6.76	9.1	17.05	22.5	72.5
Distribution coefficient of Au(III) ion	14076	11313	10087	6797	6890	2137

(c)

Figure 1. (a) Effect of acidity to the gold (III) sorption (▪HCl, ■H_2SO_4, ▲HNO_3); (b) effect of adsorbent dose; (c) calculated results of Au (III) distribution coefficient in solution.

respectively. These peaks match well with the d spacing of pure metallic gold in cubic Fm3m space group. From the XRD pattern we indicate the characteristic diffraction peaks for nanogold particles which consist as a single phase in the polymer matrix. The XRD pattern reveals the peaks with characteristic d spacing for pure metallic gold as obtained from JCPDS-International Center for Diffraction Data. The results are in good agreement with the literature report [18] [19]. Elemental crystals size of the average price consisting gold particles were calculated by special program (Evaluation) on the basis of the X-ray analysis results. It was found that the average particle size of elemental gold crystals is 28.31 nm. The obtained results indicate that nanoparticles agglomerate and form to the gold particles in polymer matrix due to reduction of Au (III) ions by thiourea reagent.

Based on the obtained results and the date reported earlier, using thiourea non covalent immobilizated polymer sorbent for the uptake of Au (III) ions from aqua media, the pure gold particles embedded in nano form in the polymer matrix. Thus, the presence of pure metal-nanogold in the polymer matrix could be confirmed.

This result was also confirmed from the Scanning electron microscope (SEM), Energy Dispersive Spectroscopy (EDS) investigation. **Figure 3** shows the SEM image of the gold nanoparticles in polymer matrix. The

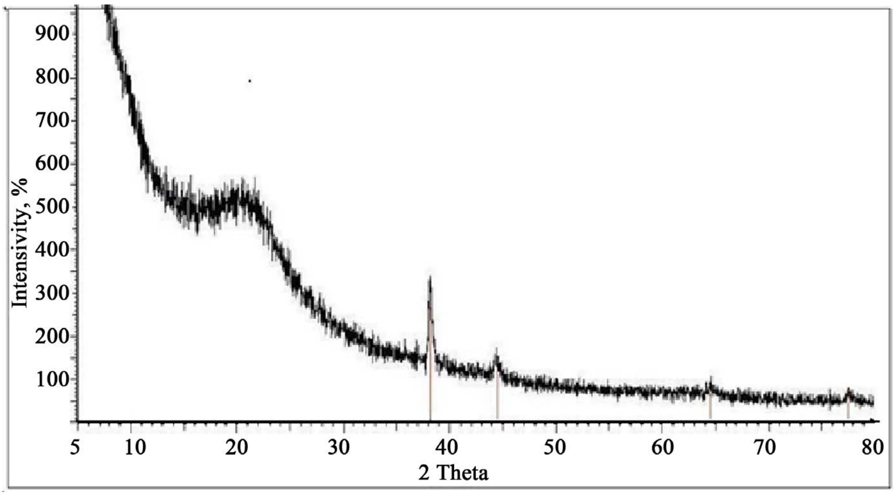


Figure 2. X-ray diffraction pattern of nanogold embedded polymer matrix.

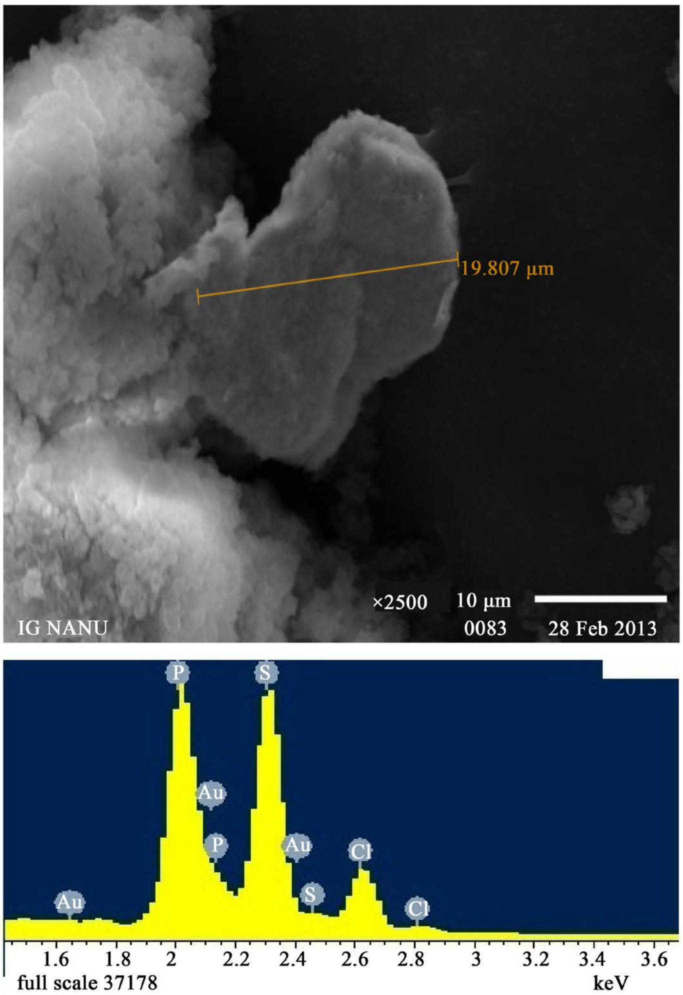


Figure 3. SEM image and EDS spectra of gold particles embedded polymer matrix.

SEM micrograph with of 3000× (**Figure 3**) shows the presence of gold particles in the surface of the polymer matrix. A similar result has been reported in [20] [21]. In addition, energy dispersive X-ray (EDS) measurements and quantitative elemental analyze made on the sample shows the expected primary metal signals along with weak S signals, which suggests the presence of sulfur-containing reagent in reduction of gold. Gold nanoparticles were immobilized into the pores of polymer by shaking it with aqueous solution containing $H[AuCl_4]^-$ complex.

These results support that the sequential process comprising of the loading of polymer sorbent followed by sorption of gold ions, could be an alternative method for recovery of metallic zero-valent gold from the gold solution.

4. Conclusion

The use of polymeric sorbent is able to sorb not only heavy metals, but also gold (III) ions as a result of the treating of thiourea solutions with the same sorbent. The polymeric sorbent is produced on the basis of chemical modification of industrial synthetic butadiene rubber SBR, as a result of the oxidative chlorophosphorylation reaction. The thiourea loaded polymeric sorbent permits uptake of gold (III) ions from the aquous solution effectively. The SEM, XRD, EDS investigations show that after sorptional process, Au (III) ions converted to a gold nanoparticles in the pores of polymer sorbent. The developed method could be extended for further applications on the low-cost procedures for the quantitative uptake of gold ions and formation of gold nanoparticles in the polymer matrix. We contemplate that our produced nanocomposite material has a large application as a catalyst in chemical reactions, sensor, and acidproof polymer materials. Work is continuing to investigate the influence of size of gold particles to the physic and chemical properties of nanocomposities.

Acknowledgements

This investigation work supported by the Department Chemistry in BSU, Institute of Geology of NASA, Analytical Centre laboratories. Authors would like to thank Dr. Azer Amirov for XRD results, Dr. Mamedali Abdullayev, Shafaq for SEM micrograph.

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