Short Communication

Chemically modified polymer beads for sorption of gold from waste gold solution

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ABSTRACT

A simple method to convert gold from waste gold solutions used in chemical laboratories and chemical industries into metallic gold nano particles using styrene maleic acid copolymer beads has been approached. The styrene maleic acid copolymer beads with an average bead diameter 400–600 microns, exhibiting exceptionally high rough surface was used as a polymer matrix for the reducing gold from aqueous solution to metallic nano gold. Uptake of gold ions from aqueous waste gold solution was attempted in a batch process. Conversion of gold to metallic nano gold was achieved without the use of any external reducing agents. The metallic nano gold particles could be embedded into polymer matrix within 2 h. The beads exhibited high temperature resistance and could sustain upto 400 °C.

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1. Introduction

Nanogold aggregates and gold nano particles have attracted attention due to their potential and practical applications as nanoelectronic devices, catalyst, biological sensors [1–9] etc. The applications of gold nanoparticles to detect analytes based on optical and electronic methods are a hot area of research [10–14]. The ability of gold to produce heat after absorbing light provides medicinal usage with applications in gene and drug delivery [15]. With the conventionally used methods, synthesis of gold nanoparticles by physical methods provides nanoparticles in a narrow range but requires the use of expensive equipments and has low yield. The hazardous effects of organic solvents, reducing agents and toxic reagents used for gold nanoparticles synthesis has encouraged researchers to develop alternative methods for preparation of nanogold [16,17]. Uptake of Au(III) ions from aqueous solutions onto chitosan, bagasses ash, bacterias, durio zibethinus husk, activated carbon etc. have been reported in the literature [18–22]. Here we report the novel method for synthesis of pure form of gold in nano size which is stable when heated upto 100 °C. This nano form of pure gold was synthesized in the polymer matrix without the use of external reducing agents. The affinity of the polymer to bind chemically with the bulk gold from aqueous solution and slowly reduce it to nano form has been empowered. The concentration of the gold solution plays a key role in determining the

size of the nanoparticles. The nanogold embedded polymer matrix was found to be stable to concentrated acids and alkalis, UV light and could sustain upto 600 °C. This simple and versatile polymer matrix thus innovatively converts gold from waste gold solutions from the chemical laboratories and chemical industries into gold nanoparticles which are the purest form of gold.

2. Methods

In a typical synthesis, 36 ml styrene, 42 ml divinyl benzene and 50 g maleic anhydride were vigorously stirred in a reaction vessel with aqueous solution of in situ formed $Mg(OH)_2$, saturated with NaCl to form spherical crosslinked styrene-maleic anhydride polymer which was then hydrolyzed to form crosslinked styrene-maleic acid (SMA) polymer. This polymer was purified by continuous soxhlation to remove adhering salts and dried at 50 °C under vacuum to constant weight [23]. The synthesized SMA polymer was colourless and stable upto 400 °C.

Mimicked gold solution was prepared by dissolving chloroauric acid ($HAuCl_4$) in deionized water. The pH of the stock solution prepared by dissolving 0.5 g chloroauric acid in 1000 ml deionized water was found to be 6.5. Chloroauric acid solution of 100 mg/l, 250 mg/l and 500 mg/l Au(III) ions were prepared by diluting the stock solution, which showed characteristic UV peaks at 310 nm. Uptake of gold ions from 20 ml Au(III) solution using 0.5 g of polymer was monitored by examining the decrease in 310 nm peak. Complete disappearance of the 310 nm peak was observed within 4 h. The polymer was left in the solution for further 24 h. Slow reduction of Au(III) to Nanogold was observed which changed the

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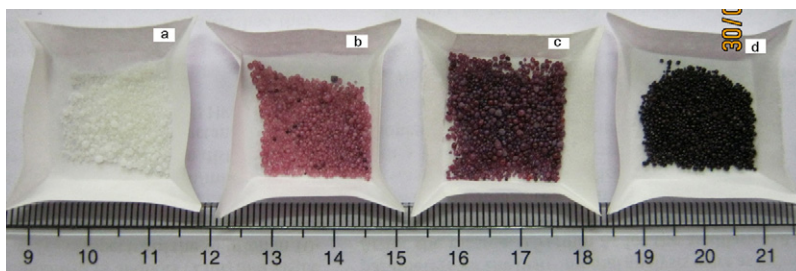
Fig. 1. A representative range of polymer matrix coloured with gold nanoparticles (a) SMA beads and (b–d) nanogold embedded SMA beads.
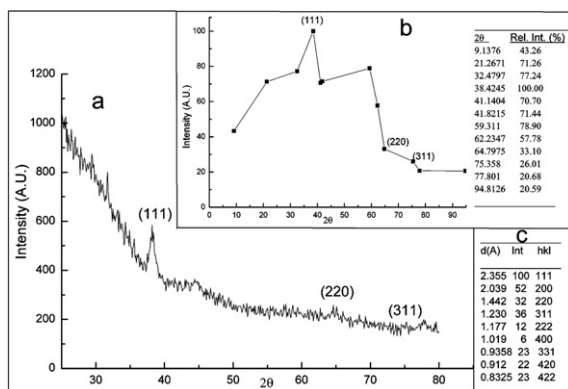

Fig. 2. (a) X-ray diffraction pattern of nanogold embedded polymer matrix; (b) characteristics peaks and (c) d spacing of pure metallic gold.

colour of the polymer to pink, purple and blue-black depending on the concentration of Au(III) solution used. The wide range of colour displayed by the polymer matrix with adsorbed nanogold particles is shown in Fig. 1(a–d).

3. Results and discussions

The XRD pattern for the nanogold embedded polymer matrix is shown in Fig. 2a. Fig. 2b shows the observed characteristic peaks for nanogold embedded polymer matrix and Fig. 2c shows the characteristic d spacing for pure metallic gold as obtained from JCPDS-International Center for Diffraction Data. The XRD pattern reveals the peaks with d spacing of 2.34279, 1.43883 and 1.26127 Å, which are indexable as (1 1 1), (2 2 0) and (3 1 1) reflections respectively in a cubic space group. These peaks match well with the d spacing of pure metallic gold in cubic $Fm\bar{3}m$ space group. The appearance of these diffraction peaks indicates the presence of pure
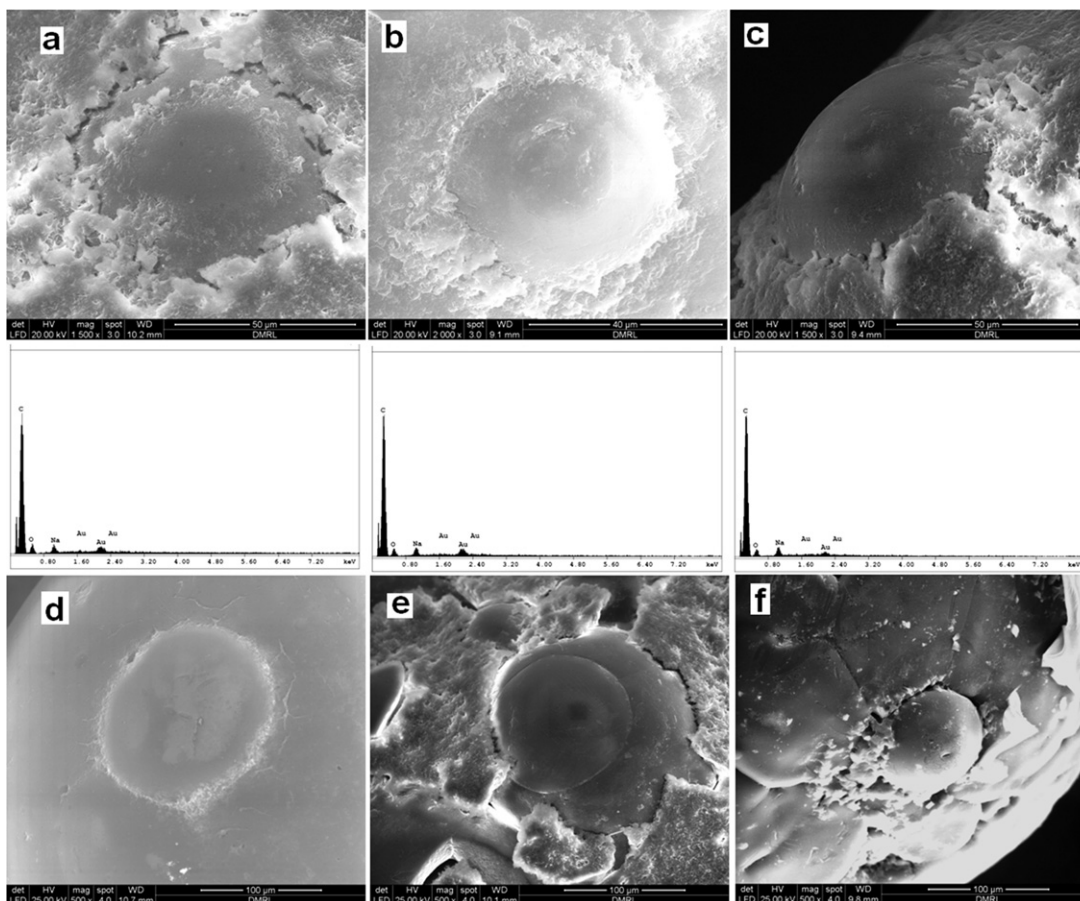
Fig. 3. SEM images of nanogold embedded polymer matrix formed using (a) 100 mg/l Au(III) solution, (b) 250 mg/l Au(III) solution and (c) 500 mg/l Au(III) solution. Heat treated nanogold embedded polymer matrix at (d) 200 °C, (e) 400 °C and (f) 600 °C.
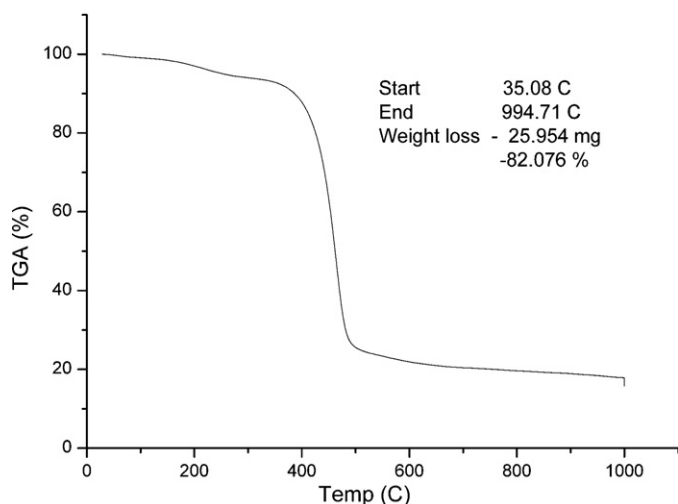
Fig. 4. TGA graph of crosslinked SMA polymer.

gold in nano form embedded into the polymer matrix. This is also confirmed from the scanning electron microscopic (SEM) images and EDS spectra's obtained for these samples.

Fig. 3(a–c) shows the SEM images of the gold nanoparticles embedded polymer matrix. In addition, energy dispersive X-ray spectroscopy (EDS) measurements and quantitative elemental analysis made on each sample shows the expected primary metal element signals along with weak Na signals, which suggests the role of Na ions in reduction of gold. The EDS spectra's obtained are shown below respective SEM images. The SEM micrographs with magnification of 5000× (Fig. 3a–f) show the presence of gold nano particles bound to the surface of the polymer matrix. The micrographs also indicate the scattered nanoparticles present on the surface in high concentrations around the micro fissures and micro voids. The polymer exhibits the pink, purple and blue black colouration even though the particles cover only a fraction of polymer. This may be because of high extinction coefficient of gold under surface Plasmon resonance conditions. The results are in good agreement with the literature report [24].

To confirm the presence of pure metallic gold, the nanogold embedded polymer beads were heated between 200 °C and 600 °C. The change in the colour of the polymer matrix (pink, purple and blue-black) to black indicates that the nanoparticles agglomerate during the process of heating which could be reflected from the SEM images (Fig. 3d–f). The styrene maleic acid copolymer being thermostable upto 500 °C (as observed from the TGA graph (Fig. 4)), no dimensional change in the polymer was observed. The EDS graph of such heat treated nanogold embedded polymer matrix also showed the presence of gold peak. Thus the presence of pure metallic nanogold in the polymer matrix could be confirmed. Heating the polymer matrix above 600 °C caused complete decomposition of the sample hence; further heating was not carried out.

The Fourier Transform Infrared spectrum of the polymer and nanogold embedded polymer is shown in Fig. 5. The resonance stabilized carboxylate anions peaks were observed at $1600\,cm^{-1}$ and $1400\,cm^{-1}$. The aromatic –C–H stretching frequency at $3024\,cm^{-1}$ was also noted. The presence of para substituted benzene was confirmed from the –C=C– stretch at $1450\,cm^{-1}$ and two bands near $1600\,cm^{-1}$[25]. The free acid peak corresponding to the reaction between chloroauric acid and SMA polymer was observed at $1639\,cm^{-1}$, which suggests the initial chemisorptions of gold followed by simultaneous reduction to nano form. Thus it can be presumed that the interaction is through the carboxyl group of maleic acid to stabilize the gold nanoparticles. The schematic representation of the process and predicted mechanism is shown in Fig. 6.

The adsorption efficiency was studied varying the initial concentration, pH of the gold solution and amount of sorbent at 27 °C for an initial period of 60 min. The results showed pronounced effect of solution pH on uptake of Au (III) ions from aqueous solutions. Effective adsorption was observed at pH 6.5 (Fig. 7a). Increasing the concentration of the gold ions in the solution showed the decrease in the adsorption efficiency which can be attributed to the saturation of active sites on the polymer surface (Fig. 7b). Adsorption efficiency however increased with increase in the sorbent amount form 0.1 g to 0.5 g. This increase in the uptake is due to the increase in the active adsorption site contributed by additional amount of sorbent. No significant increase in the adsorption efficiency was observed with use of sorbent beyond 0.5 g (Fig. 7c).
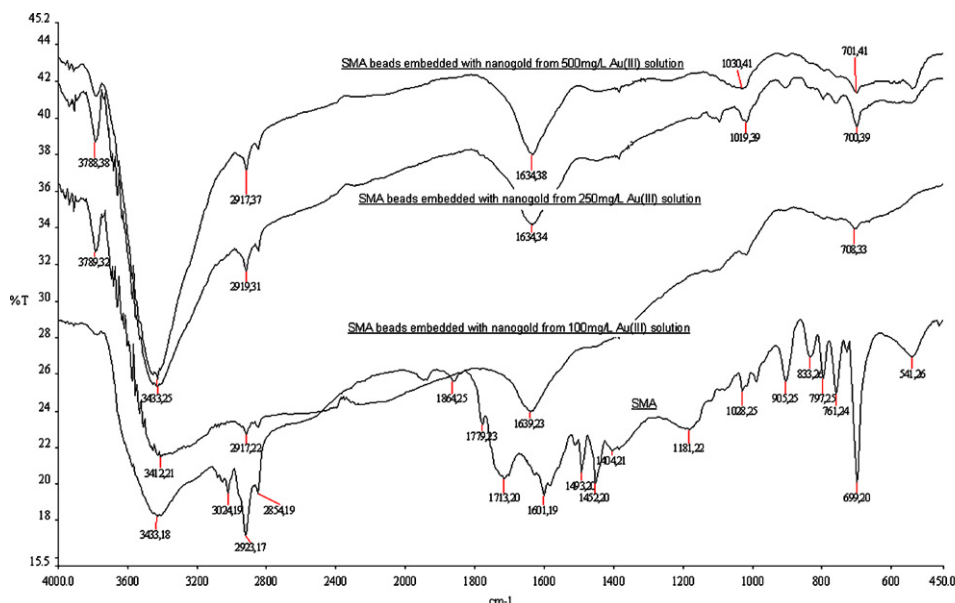

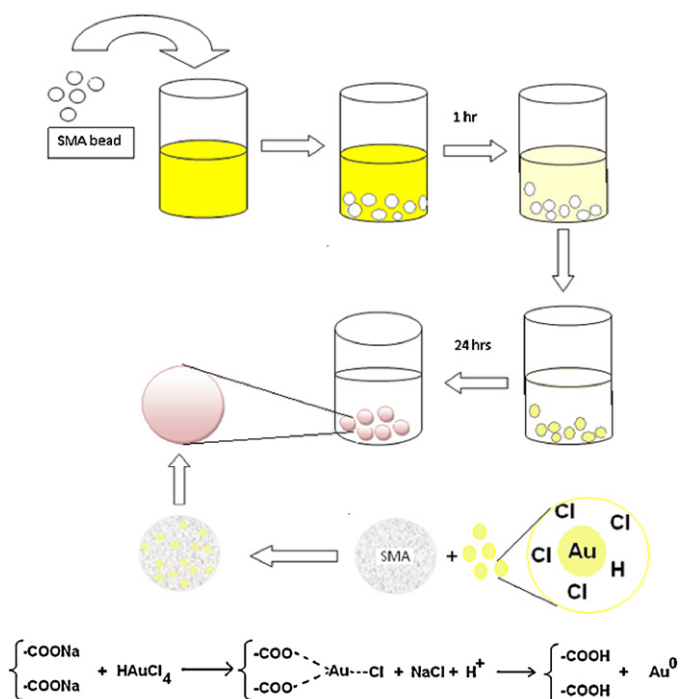**Fig. 5.** FTIR spectrum of polymer and nanogold embedded polymer.

Fig. 6. Schematic representation of adsorption and reduction of gold to nanogold onto polymer matrix.

The efficiency of adsorption was validated by applying the Freundlich adsorption isotherm model which considers the multilayer adsorption onto heterogeneous surface. The Freundlich equation [26]:

$$qe = K_F Ce^n \qquad (1)$$

where qe and Ce are equilibrium concentration of gold ions in adsorbent (mg/g) and liquid phase (mg/l). K_F and n are the Freundlich constants. The linearized equation takes the form:

$$\ln qe = \frac{1}{n} \ln Ce + \ln K_F \qquad (2)$$

The plot of ln qe versus ln Ce as shown in Fig. 7(d) presented the value of n to be 2.45 which indicate the favorable adsorption and strong interaction between the gold ions and the polymer matrix. The isotherm parameters are shown as insert in Fig. 7(d) clearly indicates that the equilibrium adsorption isotherm can be very well described by Freundlich model. The dynamics of adsorption process in terms of order and rate constants were evaluated using the pseudo second order kinetic adsorption model as described by Ho [27]

$$d\frac{qt}{dt} = k_2 (qe - qt)^2 \qquad (3)$$

where k_2 (g mg^{-1} min^{-1}) is the second order rate constant. The integrated form of the Eq. (3) is

$$\frac{1}{qe - qt} = \frac{1}{qe} + k_2 t \qquad (4)$$

Rearranging Eq. (4) gives,

$$\frac{t}{qt} = \frac{t}{qe} + \frac{1}{k_2 qe^2} \qquad (5)$$

the plot of t/qt versus t as shown in Fig. 7(e) yielded the second order rate constant k_2, equilibrium capacity qe and regression coefficient (R^2) for initial Au(III) concentration varying from 100 to 500 mg/l. The calculated values as presented in Fig. 7(f) shows good agreement with the experimental values and obtained regression coefficient values indicates that the pseudo second order kinetic model describes well the adsorption of Au(III) ions using SMA polymer as adsorbent. Adsorption of transition metal ions like Cu(II), Ni(II), Zn(II)) using various adsorbents reported in literature suggests favorable Freundlich adsorption mechanism and rate of
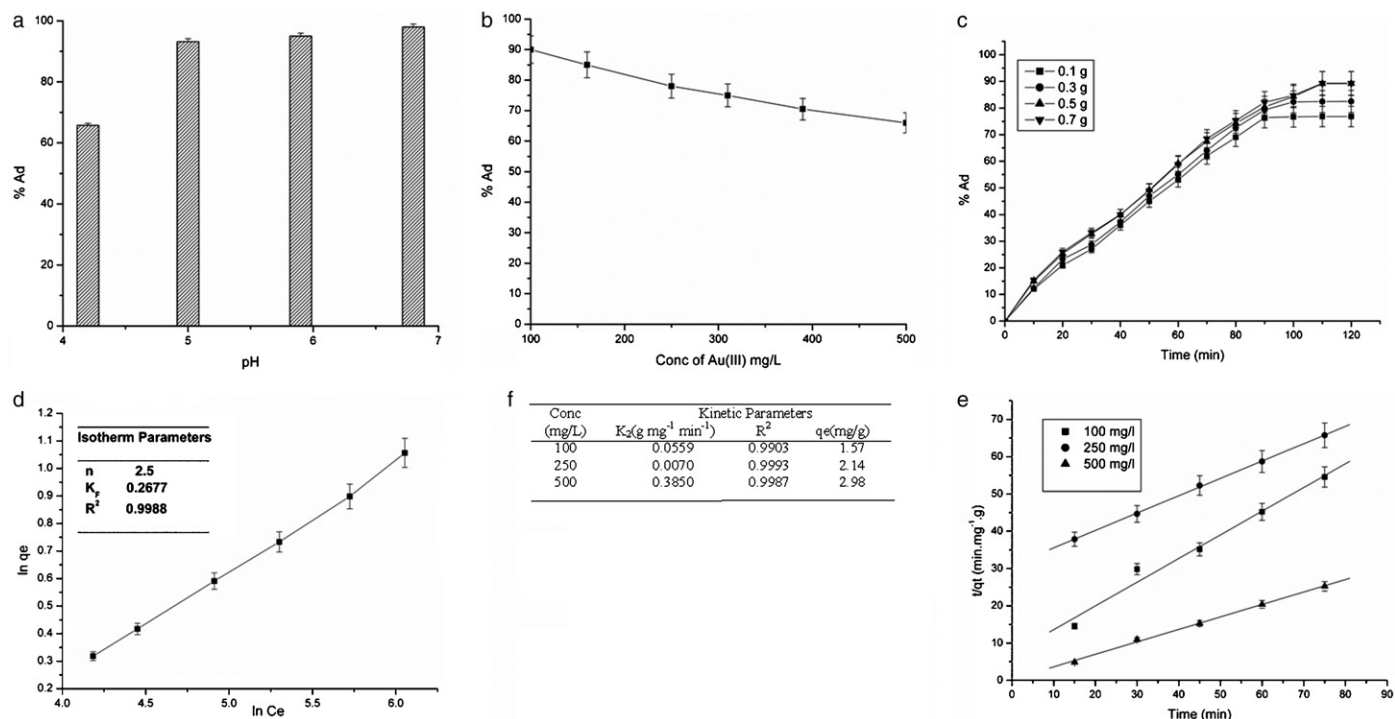

Fig. 7. (a) Effect of solution pH; (b) Effect of initial solution concentration; (c) effect of adsorbent dose; (d) Freundlich adsorption isotherm plot; insert shows Freundlich isotherm parameters; (e) pseudo second order model and (f) pseudo second order kinetic parameters.

adsorption could be well described by pseudo second order rate equation [28–30].

4. Conclusions

The previous work on nanogold synthesis is mostly with the help of toxic reducing agents and capping agents like sodium borohydride, stannous chloride, ascorbic acid, TX-100 (Triton X-100 $(C_{14}H_{22}O(C_2H_4O)_n)$), ethylene glycol, cetyltrimethylammonium bromide, which results in formation of gold nanoparticles but do not ensure the purest form of metallic gold. We have adopted a procedure that can reduce gold to its metallic nano form and simultaneously entrap it into the polymer matrix, without the use of any addition reagents. We anticipate that with this polymer the formation of metallic gold nanoparticles is possible using the spent wastewater. Such polymer can find excellent potential applications in gold coating industries. Such gold loaded polymer being stable to acidic conditions can also find potential application as catalyst in highly selective chemical transformation, biomedical applications.

Acknowledgements

References

[1] D.L. Feldheim, K.C. Grabar, M.J. Natan, T.E. Mallouk, Electron transfer in self-assembled inorganic polyelectrolyte/metal nanoparticle heterostructures, J. Am. Chem. Soc. 118 (1996) 7640–7641.

[2] U. Simon, G. Schön, G. Schmid, The application of Au$_{55}$ clusters as quantum dots, Angew. Chem. Angew. Chem. Int. Ed. Engl. 32 (1993) 250–254.

[3] H. Huber, D. McIntosh, G.A. Ozin, A metal atom model for the oxidation of carbon monoxide to carbon dioxide. The gold atom–carbon monoxide–dioxygen reaction and the gold atom–carbon dioxide reaction, Inorg. Chem. 16 (1977) 975–979.

[4] M.M. Maye, J. Luo, Y. Lin, M.H. Engelhard, M. Hepel, C.J. Zhong, X-ray photoelectron spectroscopic study of the activation of molecularly-linked gold nanoparticle catalysts, Langmuir 19 (2003) 125–131.

[5] G. Schmid, S. Emde, V. Maihack, W. Meyer-Zaika, St Peschel, Synthesis, catalytic properties of large ligand stabilized palladium clusters, J. Mol. Catal. A 107 (1996) 95–104.

[6] A. Sanchez, S. Abbet, U. Heiz, W.D. Schneider, H. Haekkinen, R.N. Barnett, U. Landman, When gold is not noble: nanoscale gold catalysts, J. Phys. Chem. A 103 (1999) 9573–9578.

[7] U. Heiz, A. Sanchez, S. Abbet, W.D. Schneider, Tuning the oxidation of carbon monoxide using nanoassembled model catalysts, Chem. Phys. 262 (2000) 189–200.

[8] M. Valden, X. Lai, D.W. Goodman, Onset of catalytic activity of gold clusters on titania with the appearance of nonmetallic properties, Science 281 (1998) 1647–1650.

[9] H. Wohltjen, A.W. Snow, Colloidal metal–insulator–metal ensemble chemiresistor, Sensor Anal. Chem. 70 (1998) 2856–2859.

[10] Z. Zhong, K.B. Male, J.H.T. Luong, More recent progress in the preparation of Au nanostructures properties, and applications, Anal. Lett. 36 (2003) 3097–3118.

[11] L.M. Ao, F. Gao, B.F. Pan, R. He, D.X. Cui, Fluoroimmunoassay for antigen based on fluorescence quenching signal of gold nanoparticles, Anal. Chem. 78 (2006) 1104–1106.

[12] Y.C Cao, R.C. Jin, J.M. Nam, C.S. Thaxton, C.A. Mirkin, Raman-dye-labeled nanoparticle probes for proteins, J. Am. Chem. Soc. 125 (2003) 14676–14677.

[13] J. Burmeister, V. Bazilyanska, K. Grothe, B. Koehler, I. Dorn, B.D. Warner, E. Diessel, Single nucleotide polymorphism analysis by chip-based hybridization and direct current electrical detection of gold-labeled DNA, Anal. Bioanal. Chem. 379 (2004) 391–398.

[14] E. Diessel, K. Grothe, H.M. Siebert, B.D. Warner, J. Burmeister, Online resistance monitoring during autometallographic enhancement of colloidal au labels for DNA analysis, Biosens. Bioelectron. 19 (2004) 1229–1235.

[15] M. Shakibaie, H. Forootanfar, K. Mollazadeh-Moghaddam, Z. Bagherzadeh, N. Nafissi-Varcheh, A.R. Shahverdi, M.A. Faramarzi, Green synthesis of gold nanoparticles by the marine microalga *Tetraselmis Suecica*, Biotechnol. Appl. Biochem. 57 (2010) 71–76.

[16] I. Maliszewska, L. Aniszkiewicz, Z. Sadowski, Biological synthesis of gold nanostructures using the extract of *Trichoderma koningii*, Acta Phys. Pol. A 116 (2009) S163–S165.

[17] P. Mukherjee, S. Senapati, D. Mandal, A. Ahmad, M.I. Khan, R. Kumar, M. Sastry, Extracellular synthesis of gold nanoparticles by the fungus *Fusarium oxysporum*, Chem. Biol. Chem. 3 (2002) 461–463.

[18] G. Hussain, M. AliKhan, Adsorption of gold (III) from aqueous solutions on bagasse ash, J. Chem. Soc. Pak. 33 (2011) 317–323.

[19] A. Hafeez, U. Ali, M. AliKhan, Recovery of gold from electroplating waste water effluents by using orange peel, J. Chem. Soc. Pak. 32 (2010) 753–760.

[20] S. Huiping, C. Huaigang, L. Xingang, C. Fangqin, Kinetics and modelling of biomagnetic separation of Au(III) from wastewater, Adv. Mater. Res. 233 (2011) 1031–1035.

[21] W.S. WanNgah, K.H. Liang, Adsorption of gold(III) ions onto chitosan and N-carboxymethyl chitosan: Equilibrium studies, Ind. Eng. Chem. Res. 38 (1999) 1411–1414.

[22] M. Soleimani, T. Kaghazchi, Adsorption of gold ions from industrial wastewater using activated carbon derived from hard shell of apricot stones- an agricultural waste, Bioresour. Technol. 99 (2008) 5374–5383.

[23] R. Gonte, Balasubramanian K., P.C. Deb, P., Singh, Synthesis and characterization of mesoporous hypercrosslinked poly (styrene co- maleic anhydride) microspheres, J. Poly. Mater., in press.

[24] J.H. Johnston, K.A. Lucas, Nanogold synthesis in wool fibres: novel colourants, Gold Bull. 44 (2011) 85–89.

[25] W. Kemp, Organic spectroscopy, in: Infrared Spectroscopy, third edition, Palgrave Macmillan, 1991.

[26] Y.H. Li, Z. Di, J. Ding, D. Wu, Z. Luan, Y. Zhu, Adsorption thermodynamics, kinetics and desorption studies of Pb^{2+} on carbon nanotubes, Water Res. 39 (2005) 605–609.

[27] Y.S. Ho, Second-order kinetic model for the sorption of cadmium onto tree fern: a comparison of linear and non-linear methods, Water Res. 40 (2006) 119–125.

[28] M. Sprynskyy, B. Buszewski, A. Terzyk, J. Namiesnik, Study of the selection mechanism of heavy metal (Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+}) adsorption on clinoptilolite, J. Coll. Interf. Sci. 304 (2006) 21–28.

[29] Y. Zhang, Y. Li, X. Li, L. Yang, X. Bai, Z. Ye, L. Zhou, L. Wang, Selective removal for Pb^{2+} in aqueous environment by using novel macroreticular PVA beads, J. Hazard. Mater. 181 (2010) 898–907.

[30] F. Asadi, H. Shariatmadari, N. Mirghaffari, Modification of rice hull and sawdust sorptive characteristics for remove heavy metals from synthetic solutions and wastewater, J. Hazard. Mater. 154 (2008) 451–458.