An efficient selective reduction of nitroarenes catalyzed by reusable silver-adsorbed waste nanocomposite

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ABSTRACT

Silver nanocomposites (AgNCs) were produced by adsorption onto an electron-rich polypyrrole-mercaptoacetic acid (PPy-MAA) composite, known to be a highly efficient adsorbent for the removal of Ag^+ ions from aqueous media in the remediation of metal- contaminated water sources. In situ reduction of Ag^+ cations to Ag^0 nanoparticles (NPs) was achieved in the absence of an additional reducing agent, and the AgNCs formed were characterized by FE-SEM, EDAX, HR-TEM, STEM, XRD, ATR-FTIR, and XPS. An investigation into the potential application of these AgNCs, effectively a waste product for further processing, as a catalyst for the reduction of variously substituted nitroarenes in water was undertaken in an effort to beneficiate the materials and determine the reaction's specificity. One composite having 11.14 ± 0.05 wt% Ag content was particularly active in these reductions, with aniline derivatives being prepared in 71–94% yields. The kinetics of the reaction was examined using 4- nitrophenol, a common water-soluble pollutant; pseudo-first-order kinetics was observed with predicted activation energy of 68.3 kJ/mol for this system. Furthermore, this AgNC displayed superior stability over 10 reaction cycles without loss of catalytic activity. A mechanism was elucidated based on these findings. The mild, economical, and efficient reduction method using a reusable "waste" material may prove a promising alternative for further industrial application.

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1. Introduction

In recent years, the use of heterogeneous catalysts to promote the efficiency and the sustainability of reactions in organic synthesis has aroused considerable attention [1–3]. Additionally, principles such as waste minimization, the use of metal-incorporated waste material as catalysts, performing reactions open to the atmosphere at ambient temperature and pressure are key considerations [4–6]. In particular, the use of a retrievable catalyst from a reaction using water as solvent is highly attractive from an environmental standpoint [7]. From the point of view of the catalyst, the use of solid supports [8–13], such as activated carbon [8,9], polymers [10], alumina [11], zeolites [12], and TiO_2 [13] have conferred increased stability, reactivity, selectivity, and reusability of specifically metal nanoparticles. Such metal nano-materials [14–16] and other bimetallic nanocatalysts [17–20] have been widely employed in various catalytic protocols.

Substituted aromatic amines are versatile important building blocks in preparation of fine chemicals, pigments, dyes, agrochemicals, pharmaceuticals, and biotechnology [21,22]. In addition, they form the basis of many common chemical intermediates such as amides, azo compounds, diazonium salts, and imines [23]. Aromatic amines are commonly prepared by catalytic reduction of nitroarenes using noble metal complexes and metal nanoparticles derived from Rh [24,25], Ru [26], Pt [27,28], Pd [29,30], Au [31], Ag [32], Ir [33] and Ni [34] among others. These are usually used in combination with hydrazine, CO/H_2O, alcohols, ammonium formate, hydrosilanes, and sodium borohydride or ammonia borane as hydrogen sources. Additionally, stoichiometric reducing agents [35–37] derived from iron, zinc, tin and copper have been used, particularly the Fe/HCl system. Another typical method uses Raney nickel as catalyst; its pyrophoric nature, operationally com-

plex handling, and moisture sensitivity detract from its utility [38]. However, iron-catalyzed reduction systems are considered a viable alternative, due to the abundance, cost-effectiveness and lower toxicity of these catalysts. Several iron-catalyzed nitroarene reductions have been established under various conditions [39–41]. In general, however, serious environmental concerns have been raised over the use of most of these metal catalyst systems, particularly the use of acid, stoichiometric loading of reagents, lower selectivity, harsh reaction conditions, and expense associated with these materials. Another challenge associated with the reduction of nitroarenes is selectivity and compatibility with other functionality in the system. In this respect, gold catalysts have proved efficient at reducing nitro derivatives to anilines with excellent selectivitywith the associated expense [42,43] . Several methods by Beller and co-workers for the selective hydrogenation using iron catalysts with different molecular hydrogen, hydrazine hydrate, and formic acid have also been developed [44,45]. Quantitative conversion and high selectivity in these cases are offset by the need for specialized phosphine- or nitrogen-containing ligands, the use of organic solvents, and prolonged reaction time. Ranu and co-workers employed iron nanoparticles to chemoselectively reduce nitro derivatives using water as hydrogen source [46]. Recently, Bhanage et al. reported the use of a recyclable immobilized iron-based ionic liquid and hydrazine hydrate to chemoselectively and regioselectively reduce nitroarenes, albeit under reflux over a prolonged reaction time [47]. Interestingly, a readily available organocatalyst, vasicine, has been shown to chemoselectively reduce nitroarenes under metal-free and base-free conditions in water [48].

Synthetic concerns aside, from an environmental perspective, 4- nitrophenol (4-NP) is one of the most common toxic and biologically stable organic pollutants in industrial and agricultural wastewater derived from the preparation and use of dyes, pesticides and pharmaceuticals [49]. Simple reduction to 4-aminophenol (4-AP) reduces this toxicity, the product being an important structural intermediate in analgesic and antipyretic drugs, such as paracetamol and phentacin [50]. A number of catalytic reduction methods have been developed to reduce nitroarenes in order to remediate polluted wastewater streams. These include photocatalytic degradation, electrochemical methods, the electro-Fenton process, and catalytic oxidation processes [51,52]. Furthermore, several metal nanoparticles have been explored as a means to convert 4-NP to 4-AP using NaBH₄ as a generally acceptable reductant [53–55], with Pradhan and co- workers being first in reporting the use of silver nanoparticles for this purpose [56]. Hence, there is still scope for an efficient, mild and cost-effective method for nitroarene reduction in both the chemical and environmental areas utilizing sustainable heterogeneous catalysis. In this context, the catalytic hydrogenation of nitroarenes to their corresponding anilines has been investigated using reusable silver-adsorbed waste nanocomposites under mild reaction conditions.

In this present work, an efficient polymeric composite, the polypyrrole-mercaptoacetic acid incorporated polymer matrix (PPy-MAA), is reported as an excellent adsorbent for removing silver ions from aqueous streams – from the point of view of water remediation. The formation of well-structured silver nanoparticles in the matrix is demonstrated and characterized by ATR-FTIR, FE-SEM, HR-TEM, XRD and XPS techniques. In continuation of our ongoing research into the application of metal nanoparticles in catalysis [57], the silver-impregnated polymeric materials produced, effectively waste products requiring disposal, were beneficiated by applying the materials produced to the catalytic reduction of a variety of nitroarenes including 4-NP under mild reaction conditions. Catalyst performance from a kinetic, mechanistic and recyclability point of view is also considered.

2. Experimental

2.1. Chemicals

Pyrrole (Py, 99%), thioglycolic acid (mercaptoacetic acid) (≥98%), all nitro compounds, sodium borohydride (NaBH₄) and ammonium persulfate (APS) were purchased from Sigma-Aldrich, USA. Silver nitrate (AgNO₃, ≥99.0%) and acetone (ACS reagent, ≥99.5%) were supplied from Sigma-Aldrich, USA and were used as received. All the reactions were carried out in ultrapure distilled water (collected from an EASY pure®II, UV-ultrapure water system) open to atmosphere.

2.2. Preparation of PPy-MMA composite

The PPy/MAA composite was synthesized by dissolving 1.6 mL (23 mmol) mercaptoacetic acid in 60 mL of ultrapure water in a 250 mL conical flask with constant stirring at 400 rpm. Pyrrole (Py) (0.8 mL, 11.4 mmol) was added to this solution by syringe in one portion, and the homogeneous reaction was stirred for 30 min. 20 mL of ammonium persulfate (APS, 6.8 g ~30 mmol) was added dropwise to the solution and stirred for a further 6 h. Polymerization of Py was evident by the gradual development of a black composite material. The composite was filtered off and washed repeatedly with ultrapure water followed by acetone, and then dried under vacuum at 60 °C for 6 h to a constant weight. A plausible explanation for polymerization of Py monomer is based on the well- established oxidative mechanism indicating that ammonium persulphate (APS) generates free radical sites on the pyrrole backbone. These free radical sites react with another monomer and then propagate. After termination, polymer was precipitated in the ploymerization reaction medium. During polymerization, the growing PPy chain carries a positive charge on the nitrogen atoms in the reaction medium as a result of acid-base reactions with the MAA [58] . The mercaptoacetate moieties are expected to remain associated with the polypyrrole networks through electrostatic interaction, as later characterization implied.

2.3. Adsorption of Ag(I) ions onto PPy-MAA composite to form PPy- MAA/Ag nanocomposite catalyst

The adsorption of silver ions (Ag⁺) from aqueous solution was conducted in batch experiments using the PPy/MAA composite at room temperature (25 °C) while stirring at 200 rpm with an overhead stirrer. To evaluate the capacity of the PPy-MMA for Ag⁺ adsorption, five different experimental solutions, i.e. 10, 25, 50, 100 and 200 mg/L were prepared from a stock solution (1000 mg/L) of AgNO₃. For each experimental solution, 0.4 g of PPy/MAA adsorbent was added to 1 L of Ag⁺ solution at pH 5.4. After 24 h, the solution was filtered through 0.45 μm membrane filter paper and the filtrate was analyzed by ICP-MS (Thermo Fisher Scientific) to determine the residual concentration of metal ion (Ag ⁺) in the filtrate. The adsorption equilibrium capacity (q_e, mg/g) for Ag⁺ adsorption on the PPy/MAA composite was calculated using Eq. (1).

$$q_e(mg/g) = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where q_e is the adsorption capacity (mg/g) at equilibrium; C_0 and C_e are the initial and the equilibrium concentrations (mg/L) of Ag⁺ ions respectively; V is the volume of the experimental solution (L), and W is the weight of the adsorbent (g). The PPy-MAA/Ag⁺ composite was collected for use in the reduction of 4-NP. Five different catalysts having different wt% of silver were collected these processes: Ag NC-1 (11.14 ± 0.05 wt%); Ag NC-2 (19.75 ± 0.05 wt%); Ag NC-3 (32.51 ± 0.05 wt%); Ag NC-4 (5.83 ± 0.05 wt%); Ag NC-5 (2.42 ± 0.05 wt%). From XRD, XPS, FE-SEM and HR-TEM studies, it