



# Cationic microgels embedding metal nanoparticles in the reduction of dyes and *nitro*-phenols



Saif ur Rehman<sup>a</sup>, Mohammed Siddiq<sup>a</sup>, Hamad Al-Lohedan<sup>b</sup>, Nurettin Sahiner<sup>b,c,d,\*</sup>

<sup>a</sup> Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan

<sup>b</sup> Surfactants Research Chair, Department of Chemistry, College of Science, King Saud University, P.O. Box-2455, Riyadh 11451, Saudi Arabia

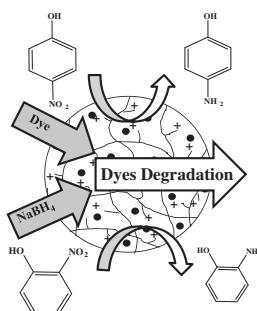
<sup>c</sup> Chemistry Department, Faculty of Science and Arts, Canakkale Onsekiz Mart University, Terzioğlu Campus, 17100 Canakkale, Turkey

<sup>d</sup> Nanoscience and Technology Research and Application Center (NTRAC), Canakkale Onsekiz Mart University, Terzioğlu Campus, 17100 Canakkale, Turkey

## HIGHLIGHTS

- Inherently cationic p(APTMACI) microgels via inverse suspension polymerization.
- P(APTMACI)-M (M: Co, Ni, Cu) metal nanoparticle composite catalyst preparation.
- High effective p(APTMACI)-M catalyst in nitrophenolic compound reductions.
- High effective p(APTMACI)-M catalyst in eosin Y and methyl orange reduction.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Cationic microgels of p(3-Acrylamidopropyl)-trimethylammonium chloride (p(APTMACI)) were synthesized using the inverse suspension polymerization technique, and the obtained microgels were used as microreactor for *in situ* synthesis of Co, Ni, and Cu nanoparticles. The p(APTMACI) microgels were loaded with Co, Ni, and Cu after contact with chloride salts of the metals,  $\text{CoCl}_2$ ,  $\text{NiCl}_2$ , and  $\text{CuCl}_2$ , in ethanol and reduced to their respective metal nanoparticles by treating them with sodium borohydride ( $\text{NaBH}_4$ ) as reducing agent. The metal nanoparticle content of p(APTMACI) microparticles were quantified for each composites by atomic absorption spectroscopy (AAS) after dissolution of the metal nanoparticles within microgel composites by concentrated hydrochloric acid (HCl). Dynamic light scattering (DLS) was used to monitor zeta potential of the microgel composites. Thermal properties of both cationic p(APTMACI) microgel and its composites were investigated with a thermal gravimetric analyzer (TGA). It was also found that the p(APTMACI) composites performed as excellent catalyst systems in the reduction of different aromatic pollutants like 2-nitrophenol, 4-nitrophenol and fluorescent dyes like eosin Y (EY), and methyl orange (MO). Various parameters such as metal types, and their respective amount, and temperature were investigated to determine the catalytic performances of the microgel-metal nanoparticle composites.

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## 1. Introduction

With the onset of the industrial revolution, severe setbacks to human health and eco systems have occurred as a consequence

of the discharge of dangerous industrial pollutants into the environment. In general, textile industries, printing, iron-steel, petroleum, pesticides, paint, pharmaceuticals and so on where a large diversity of solvent and organic based chemicals are used, may

\* Corresponding author at: Chemistry Department, Faculty of Science and Arts, Canakkale Onsekiz Mart University, Terzioğlu Campus, 17100 Canakkale, Turkey.

contaminate surface, ground and lake/sea water. These waters become contaminated by a vast variety of organic and inorganic contaminants. Of these, the aromatic nitro compounds particularly nitrophenols, and artificial dyes are of critical concern on account of their poisonous and cancer inducing nature [1]. The major aromatic nitro compound pollutants are mainly nitrophenols in industrial and agricultural waste waters as they are soluble and stable for a long time in water. Because of their harmful nature, the U.S. Environmental Protection Agency has listed nitrophenols as pollutant materials [2]. They have also been reported as a major concern in poisoning aquatic life. Additionally, these pollutants can cause odor problems in water reservoirs [3]. Therefore, to protect the environment, the removal of nitrophenols and other organic pollutants from industrial wastewaters has vital significance. Nevertheless, as they are biologically and chemically stable, nitrophenols cannot be easily removed through natural microbial degradation defense systems [4].

Similarly, textile industry wastes are considered one of the main sources of water pollution throughout the world as dyes are vastly colored and are resistant to decay. Azo dyes comprise almost half of world production, nearly 15% of which is reported to end up in polluted waters during dyeing operation processes [5]. Aromatic azo-dyes occupy nearly half of the global dye market [6]. Azo-dyes also compose the main group of synthetic organic compounds discharged by a number of industries such as paper, plastic, leather, food, cosmetic and pharmaceutical industries [7]. Moreover, azo-dye compounds are identified as prospective carcinogens [8], and contaminated waste water treatment necessitates the reduction or removal of these dyes.

Biological stains such as eosin-Y, auramine-O, hematoxylin, and rose Bengal are widely used in biomedical research laboratories and also for diagnostic purposes. It has been observed that to a degree these stains are poisonous or mutagenic for both human and animals [9]. Though, the stain solution amounts used in laboratories are comparatively small, the high potency of dyes consequently forms toxic waste water with decreased light transparency and increased amounts organic carbon content. Eosin Y, a heterocyclic dye, contains bromine atoms and is extensively used as a counter stain in everyday staining of histological tissue sections like erythrocytes, collagen, and epithelial cells. Additionally, it is used in printing, dyeing, leather and fluorescent pigment, etc. Waste water containing eosin Y, on direct release, leads to severe environmental hazards on account of its dark color and toxicity [10].

The dye discharging industries cause water pollution, and the polluted waters when brought in contact with living tissue over a long time, are harmful. Releasing dyes and toxic organics into the rivers, stream, creeks and lakes without proper treatment causes irreversible harmful effects to both aquatic and terrestrial crops and living organisms. This necessitates the development of environmentally friendly and effective methods for removing such contaminants from waste waters. Numerous techniques, based on oxidation and reduction, have been explored for removing such pollutants such as catalytic wet air oxidation [11], photo-catalytic degradation [12], electrochemical methods [13], and hydrogenation reactions [14].

For the removal of nitrophenols and dyes from industrial waste water, one method is reduction and degradation in presence of  $\text{NaBH}_4$ . However, the reduction of nitrophenols and degradation of dyes is quite slow and takes longer times. To accelerate the process a suitable catalyst is needed using metal nanoparticles [15]. In addition to noble metals with their high cost, common metal nanoparticles such as nickel, cobalt and copper have been widely used in catalysis by various designs [15–17]. Because of agglomeration

mainly caused by excess surface energy and high thermodynamic instability of the nanoparticle surface, stabilizing agents such as surfactants, polymers and dendrimers or different templates are used for metal nanoparticle preparation [15].

Organic compound reduction reactions with  $\text{NaBH}_4$  have been reported to speed up in the presence of appropriate catalysts [18,19]. Herein, we report a comparative reduction of nitrophenols and the degradation of MO and EY dyes by using different common metal nanoparticle catalysts such as Co, Ni and Cu synthesized inside cationic p(APTMAcI) microgels. Various parameters such as temperature and various kinetic parameters are studied by using p(APTMAcI)-M in dye degradation and nitro compound reduction as a catalyst. Additionally, the degradation of dyes were carried out in different aquatic environments such as seawater, tap water and DIW.

## 2. Experimental

### 2.1. Materials

The monomer (3-acrylamidopropyl)-trimethylammonium chloride (APTMAcI, 75 wt% solution in water) was purchased from Sigma-Aldrich. The crosslinker, *N,N'*-methylenebisacrylamide (MBA, 98% Sigma), ammonium persulfate (APS, 99% Sigma) as redox initiator, and *N,N,N,N'*-tetramethylethylenediamine (TEMED, 99% Sigma) as an accelerator were used for the polymerization reaction.  $\text{NaBH}_4$  (98%, Merck) was used as reducing reagent. Cobalt(II) chloride hexahydrate ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , 99% Sigma-Aldrich), nickel(II) chloride hexahydrate ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , 97%, Riedel-de Haën) and copper(II) chloride ( $\text{CuCl}_2$ , 99% Aldrich), were used as metal ion sources for metal nanoparticle preparation. Commercial gasoline (from Shell) was used as the organic solvent for the formulation of the water in oil inverse suspension polymerization system, and the surfactant was sorbitane monooleate (SPAN<sup>®</sup>80, Fluka). Ethanol (Merck) of reagent grade was used as solvent. Distilled water (DIW, Millipore Direct-Q3 UV) was used throughout the experiments. All chemicals were used without purification.

### 2.2. Synthesis of cationic microgels

The cationic microgel particles of (3-acrylamidopropyl)-trimethylammonium chloride (APTMAcI) were synthesized by inverse suspension polymerization in gasoline using SPAN80 as stabilizing agent. Different molar ratios of the solvent and emulsifier were used to enhance the crosslinking of APTMAcI monomer to increase the yield of the microgel particles. The optimum conditions were met by keeping the emulsifier and solvent in the ratio of 1.6/10 (v/v) where the emulsifier concentration was equal to 20% of the monomer molar concentration. In this process the aqueous solution of monomer and crosslinker was prepared by taking the crosslinker of 1 mol% with respect to APTMAcI mole number. The aqueous phase was added into a mixture of gasoline (10 ml) and span 80 (1.6 ml) under stirring at 800 rpm. Then after 5 min, TEMED was added to the reaction mixture under continuous stirring. After 15 min continuous mixing, a freshly prepared solution of APS (10% to the monomer mole number) was added to initiate polymerization and crosslinking, which can be observed by the changing color of the reaction mixture. The polymerization process completed in two hours and the synthesized microgels were precipitated by adding acetone in order to remove the solvent and other unreacted species used in the reaction. The microgels were further purified through centrifugation at 10,000 rpm for 10 min each time. The purified microgels were later freeze dried and kept for further use.

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