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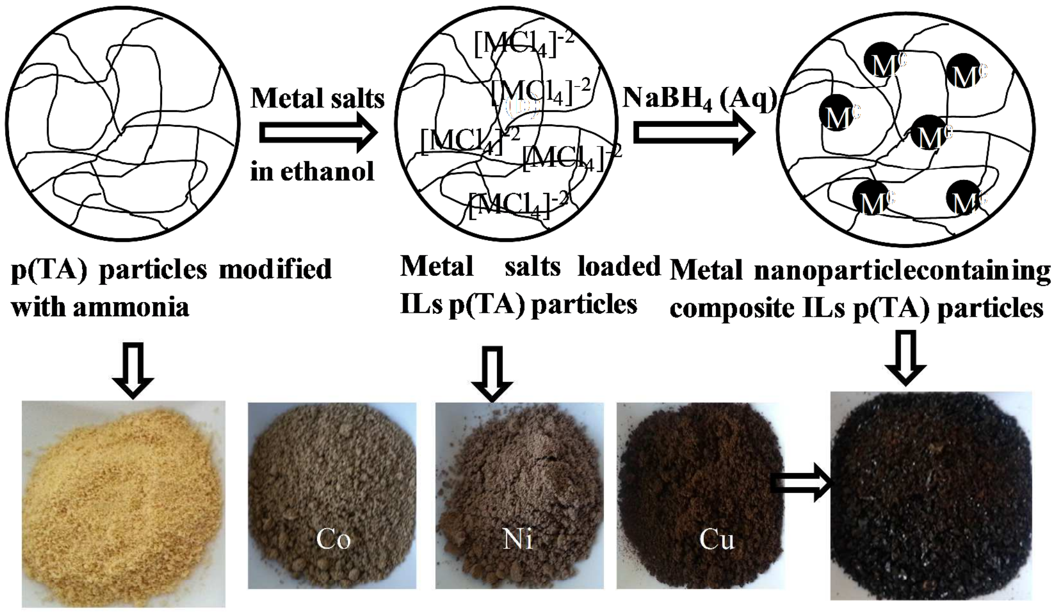
Graphical Abstract



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ARTICLE TYPE

Very fast catalytic reduction of 4-Nitro phenol, Methylene Blue and Eosin Y in natural waters using green chemistry: p(Tannic Acid)-Cu ionic liquid composites

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Using tannic acid (TA) as biopolymer, poly(Tannic Acid) (p(TA)) microgels were obtained by cross-linking TA with trimethylolpropane triglycidyl ether (TMPGDE) as cross-linker in a water-in-oil micro emulsion system. Ionic liquid forms of p(TA) micro particles were prepared as Ionic Liquid Colloids (ILC) by post chemical modification of p(TA) particles using quaternization agents such as 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPACl) and ammonia (NH_3) in aqueous solution to generate positively-charged ammonium salts on the network. Then the modified p(TA) micro particles were used as template for Co, Ni, and Cu metal nanoparticle preparation in situ after loading of metal salts such as $CoCl_2$, $NiCl_2$, and $CuCl_2$ from ethyl alcohol solution into the p(TA) network, and consequent reduction with sodium boron hydride ($NaBH_4$). The prepared metal nanoparticle-containing ILCs of p(TA) microgel composites were used as catalyst in the reduction of toxic organic compounds such as 4-nitrophenol (4-NP), eosin Y (EY), and methylene blue (MB). Various parameters affecting the 4-NP and MB reduction were investigated. The activation energy, enthalpy, and entropy for the reduction of 4-NP to 4-AP catalyzed by ILC p(TA)-Co composite catalyst system were calculated as 26.19 kJ mol^{-1}, 23.12 kJ mol^{-1}, and -182.35 J mol^{-1} K^{-1}, respectively.

1. Introduction

Ionic liquids (ILs), sometimes referred to as molten salts, consist of organic cations and organic/inorganic anions at room temperature.[1] Due to their intriguing properties, such as high thermal stability, high thermal conductivity, high polarity, high flame resistance, low interface energy, low melting points, almost zero vapor pressure and volatility related to their effective ion-ion interaction, less pollution, easily recyclable, etc.[2-4] ILs are promising materials in many applications, such as synthesis,[5] catalysis,[6] electrochemistry,[7] energy,[8] and separation.[9] Especially recently ILs have been employed in the colloid and interface sciences because their hydrophilic and hydrophobic structure can be controlled by changing the cations or anions.[10] The most common ILs consist of self-organic cations such as imidazolium, pyridinium, tetraalkylphosphonium $[C_4P]^+$, tetraalkyammonium $[C_4N]^+$, pyrrolidinium, and organic/inorganic anions such as hexafluorophosphate $[PF_6]^-$, tetraafluoroborate $[BF_4]^-$, nitrate $[NO_3]^-$ and dicyanamide $[N(CN)_2]^-$.[11]

Recently, different ionic liquid-based materials such as poly crystalline, polymers,[5] ceramics, glasses and gels[5] have been used for advanced material technology.[12,13] Micron-sized hydrogels that swell in a good solvent[14] can respond to changes in their environment or external stimuli such as temperature,[15] pH, ionic strength of the medium,[16] magnetic field,[17] electric field, and light[18] can be combined with ILs. The hydrogels with various functional groups offer unique properties, widely used for various applications such as biomedical, pharmaceutical, tissue engineering, drug delivery,[19] purification and separation,[20] biosensor,[21] and catalysis.[22,23] Biopolymers are generally derived from renewable, non-toxic, and inexhaustible natural biological resources.[24,25] Tannic acid (TA) is a common polyphenolic compound and is a natural biopolymer with strong affinity for enzymes,[26] proteins,[27,28] carbohydrates, lipids,[29] metal ions,[30] and toxic molecules[31] due to the abundant number of -OH on their phenolic structure. It is known that TA molecules can react with various metal ions such as Cu, Fe, Ni, Pd, Cr, Ar, Zn and Mn, via complex formation,[32,33] ion exchange and reduction processes.[34,35]

In addition to synthetic polymers, natural polymers can be used to create ILs properties. Therefore, herein p(TA) micro particles were synthesized using trimethylolpropane triglycidyl ether (TMPGDE) as crosslinker. The prepared p(TA) microgels were used in ionic liquid colloids of p(TA) particle preparation by exposure to various modification agents. Moreover, the prepared p(TA)-based ILs materials were used as template for in situ metal nanoparticle preparation. Some metal salts such as $CoCl_2$, $NiCl_2$, $CuCl_2$, $FeCl_2$ and $PdCl_2$ are commonly used in metal source catalysis,[8,11,36] biomedical, and environmental applications.[11,37] Therefore, modified p(TA) micro particles were interacted with Cu(II), Co(II) and Ni(II) solutions in ethanol to prepare ILCs of p(TA)-M composites (M: Co, Ni, Cu etc). The metal nanoparticle-containing composite materials provide high catalytic activity, and reusability in various applications such as hydrogen storage, fuel cell, ammonia decomposition, catalytic reform, waste water treatment, nitro compound reduction and so on.[37-43] As reported, ILs have promising potential in eliminating water pollutants such as phenolic compounds, polycyclic aromatic hydrocarbons and dyes from aquatic media.[37,38] Therefore, the synthesized ILC of p(TA)-M composite containing different metals was used as catalyst in the reduction of toxic organic compounds such as 4-nitrophenol (4-NP) and dyes e.g. MB and EY.

2. Materials and methods

2.1. Materials

Tannic acid (TA) (ACS grade, 97% Sigma-Aldrich) as monomer, trimethylolpropane triglycidyl ether (TMPGDE) (technical grade, Sigma-Aldrich) as crosslinker and L-alpha-lecithin, granular (Acros Organics) as surfactant were used as received. Gasoline as an organic solvent was procured from a local vender. The modifying agents, 3-chloro-2-hydroxypropyl trimethyl ammonium chloride solution (CHPACl, 65%, Fluka) and ammonia solution (32%, Merck) were used. Cobalt (II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, 99% Sigma-Aldrich), nickel (II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, 97%, Riedel-de Haën), and $CuCl_2 \cdot 6H_2O$ (98%, Sigma) were used as metal ion sources. Sodium borohydride ($NaBH_4$, 98%, Merck) was used for preparation of metal nanoparticles and in catalytic reduction reactions. Organic compounds such as 4-nitrophenol (4-NP, 98%, Merck), eosin Y disodium salt (85%, Sigma-Aldrich), and methylene blue hydrate (97%, Sigma-Aldrich) were used as received. Absolute ethyl alcohol (99.7%) was used for preparation of metal salt solutions and washing processes. NaOH (99%) and HCl (37.5%) were purchased from Aldrich. Seawater, Saricay (river) water, and tap water were obtained from Canakkale city in Turkey. Ultra pure distilled water 18.2 MΩ.cm (Millipore Direct-Q UV3) was used throughout the experiments.

2.2. Synthesis of tannic acid particles

Tannic acid, 2.5 g, was dissolved in 5 mL 0.2 M NaOH solution. This solution was put into 150 mL of 0.1 M lecithin in gasoline under vigorous stirring at 1200 rpm for 15 min at 50 °C. The crosslinker, TMPGDE 1.15 mL (30 mol% of gallic acid unit), as crosslinker was subsequently added as network-forming agent to this mixture under fast stirring for 12 h at 50 °C. The obtained p(TA) particles were purified by centrifugation at 35544*g* for 2 min at 20 °C. The supernatant solution was decanted and p(TA) particles were washed with cyclohexane to remove lecithin. Again, the particles were washed with ethanol two times to remove the unreacted species of TA, surfactant and crosslinker. Finally, the obtained p(TA) particles were dried with a heat gun and kept in a closed container for further use.

2.2. Preparation of modified p(TA) particles

Synthesized p(TA) particles were modified with 3-chloro-2-hydroxypropyl trimethyl ammonium chloride and ammonia aqueous solution.

2.2.1. Modification with CHPACl

To generate positive charges on p(TA) particles, 0.5 g p(TA) and CHPACl, 3 mL, were each dispersed in 15 mL 0.2 M NaOH solution, separately. These two solutions were mixed after ten minutes and stirred at 200 rpm at 50 °C for 1 h. Then, modified p(TA) particles were washed with ethanol by centrifuging, dried with a heat gun and kept in a closed container for further use.

2.2.2. Modification with ammonia

For anion exchange, 0.5 g p(TA) particles were dispersed in 30 mL ethanol containing 3 mL ammonia solution and mixed at 200 rpm for 1 h. Then, the modified p(TA) particles (p(TA) ammonium salt) were washed with ethanol again, centrifuged at 35544*g* for 2 min at 20 °C, dried with a heat gun and kept in a closed container for further use.

2.3. The in situ metal nanoparticle preparation within modified p(TA) microgel particles

For the preparation of metal salt-loaded IL p(TA) particles, 0.5 g modified p(TA) particles were placed into 1000 ppm 250 mL metal chloride salts ($CoCl_2$, $NiCl_2$, and $CuCl_2$) in ethyl alcohol for 12 h. The metal salt-loaded p(TA) particles were washed with ethanol several times to remove unbound metal salts. For the reduction of metal salts inside the particle, metal salt-loaded IL p(TA) particles were treated with 0.1 M 50 mL $NaBH_4$ solution for 2 h to reduce the metal salts to their corresponding metal nanoparticles. The prepared composite IL p(TA)-M (M:Co, Ni, Cu) particles were dried with a heat gun and kept in a closed container for further use.

2.4. Characterization of p(TA)-based particles

The p(TA) particles were imaged by scanning electron microscopy (SEM, Jeol JSM-5600 LV) by placing the particles onto carbon tape-attached aluminum SEM stubs, after coating with gold to a thickness of a few nanometers, in a vacuum using an operating voltage of 20 kV.

To determine point zero charges/pKA of particles, the pH potentiometric titration of 100 mg tannic acid (as control) and p(TA) particles were placed into 50 ml 0.01 M KCl solution, and 0.1 M NaOH solution was added drop wise under constant stirring. A change in pH was measured after equilibrium (within 10 min) within the pH range of 2-10 (Sartorius) under N_2 gas.

The functional groups of tannic acid-based materials were analyzed using FT-IR spectroscopy (Themoscientific, FT-IR 100) in the spectral range of 4000-650 cm^{-1} with a resolution of 4 cm^{-1}, using the ATR technique.

Zeta potential measurements of bare and modified p(TA) particles were conducted with a zetasizer (Zeta-Pals Zeta Potential Analyzer BIC) in 0.001 M KCl solution at different pHs in DI water.

The metal amount in ILs p(TA)-metal composites were determined by using atomic absorption spectroscopy (AAS, Thermo, ICA 3500 AA SPECTRO) and thermogravimetric analysis measurements. The thermal degradation and the metal content of ILs p(TA)-based particles were investigated using a thermogravimetric analyzer (SII TG/DTA 6300). About 5 mg of particles were placed in a ceramic crucible and the weight lost was recorded over the temperature range of 50-1000 °C at a heating rate of 10 °C min^{-1} under a dry flow of N_2 of 100 mL min^{-1}. To determine the exact amounts of M within modified p(TA)-M composites, 0.1g was treated with 10 mL 1 M HCl solution to dissolve metal nanoparticles embedded in p(TA)-M composites, and the amount of metal ions ins solutions were determined using by AAS measurements.

2.5. Reduction of 4-NP, eosin Y, and MB by p(TA)-M based composite particles

Separately, 0.01 M 4-NP, 8x10^{-4} M Eosin Y, and 3.2x10^{-4} M MB solutions were prepared and used in reduction. For the reduction of 4-NP to 4-AP, certain amounts of ILs p(TA)-M composite particles without $NaBH_4$ treatment and reduced p(TA)-M composite with $NaBH_4$ (M: Co, Ni, Cu; each 0.059 mmol) containing the same amount of metal nanoparticles were put into 0.01 M 50 mL 4-NP solution at 30±2 °C. Then, 0.4 M (0.77 g) of $NaBH_4$ was added quickly to this mixture under constant stirring rate of 800 rpm. At certain time intervals, 0.1 mL amount of this solution was taken and diluted 80 fold. The conversion of 4-NP to 4-AP reaction was monitored with the change in the intensity of 4-NP at the maximum absorption wavelength of 400 nm, and at 290 nm for the increase in the absorption maximum of 4-AP with respect to time by employing a UV-VIS spectrophotometer (T80+UV/VIS Spectrometer, PG Ins. Ltd). To investigate the kinetic parameters of the reduction of 4-NP to 4-AP, a certain amount of p(TA)-Co particles containing 0.059 mmol of metal was used as catalyst by running the reaction at five different temperatures between 30 and 70 °C under the same conditions. In order to determined the reusability of the catalysts system, the same p(TA)-Cu composite particles were used in the reduction of 4-NP five times consecutively under the same catalytic conditions one day. The composite particle was washed with DI water before each usage.

For the reduction of EY or MB, composite ILs p(TA)-M particles containing 0.0039 mmol Co, Ni, Cu nanoparticles (prepared without $NaBH_4$ treatment) was placed into 8x10^{-4} M 100 mL EY or 3.2x10^{-4} M 100 mL MB solution. Immediately, 0.075 g (2x10^{-2} M $NaBH_4$) was added to this mixture under constant stirring rate of 800 rpm. At certain times, 0.5 mL amount of this solution was removed and diluted 5 fold. Then, the reduction rate of EY or MB was measured with the change in EY (at maximum absorption wavelength 514 nm) or MB (at 664 nm) peak intensity with respect to time by employing a UV-VIS spectrophotometer. In order to determine the effect of the media on the reduction rate of EY and MB, the same molar amount of EY and MB solutions were prepared in DI water, tap water, seawater, and creek water (Saricay). Then, the reduction of EY and MB were performed under the same reaction conditions. All the experiments were done in triplicate, the mean values were calculated and the results are given with standard deviation.

3. Results and discussion

3.1. Characterization of p(TA)-based particles

It is known that TA molecules interact with metal ions due to the existence of many -OH functional groups in gallic moieties repeating groups for different purposes, e.g., in environmental applications (Figure 1a). In this study, TA molecules were crosslinked to form p(TA) microgel particles via simple micro emulsion technique with high yield (73±6%). The shape, size and size distribution of the prepared p(TA) particles were visualized by optic microscope and SEM images, and it was found that the average diameter of the particles is broad, varying between 1-5 µm represented in Figure 1b and 1c from SEM images and optical images in water, respectively. Because of the ionizable acidic nature of –OH groups, potentiometric titration of TA molecules and p(TA) particles in 0.01 M 50 ml KCl solution with 0.1 M NaOH was completed. The corresponding graph of pH versus amount of added NaOH is illustrated in Figure 1d. The potentiometric titration results indicate that TA molecules have two inflection points at pH 4.8±0.1 and pH 9.6±0.2, coming from the presence of some carboxylic groups and phenolic/hydroxyl groups, respectively[44] as gallic units are readily hydrolysable in acidic and basic environments. As supported by the literature, carboxylic groups and phenolic/hydroxyl groups have pKa values ranging from 2 to 6 and 8 to 10, respectively. However, the inflection point of p(TA) particles was found at pH 7.1±0.1 because most of the -OH groups were crosslinked with TMPGDE crosslinker.

Upon the modification of p(TA) particles with CHPACl, positive charges are generated on the p(TA) network, and upon treating with ammonia aqueous solution, ammonium salts of p(TA) particles are formed due to the neutralization of galloyl groups. Then these modified ILs p(TA) particles were used for in situ metal nanoparticle preparation. As presented in Figure 2a, some –OH groups on p(TA) particles react with the modification agent (CHPACl) with their –OH groups. Therefore, modified p(TA) particles become positively charged coming from CHPACl, or upon neutralization with NH_3 generating ammonia molecules and negatively charged pheoxylates on their structure. FT-IR spectra of p(TA) particles, and modified p(TA) particles with CHPACl and NH_3 are shown in Figure 2b. In the FT-IR spectra for p(TA) particles, a broad band at 3600-3000 cm^{-1} is due to –OH groups of polyphenols, and the peak at 1700 cm^{-1} can be assigned to C=O stretching vibrations from TA molecules. Three characteristic peaks at 1605, 1532, and 1444 cm^{-1} come from aromatic compound stretching, and the peaks at 1183, 1078, and 1016 cm^{-1} are ascribed to the vibration of substituted benzene rings.[45] The peak at 1050 cm^{-1} is due to the CH_2-O stretching because of formation ether linkage upon the crosslinking reaction. Modified p(TA) particles with CHPACl have two characteristic peaks at 1476 and 1340 cm^{-1} corresponding to C-N stretching of CHPACl molecules.[14] In the spectra of NH_3 p(TA) particles, the peak at 1430 cm^{-1} is stretching vibration coming from NH_4^+ salts on the polymer network after the modification reaction. That peak is shifted a little right in CHPACl modified p(TA) particles, as the quaternary amine groups are attached to the structure (not free). Therefore, these results demonstrate that ionic liquid colloids of p(TA) particles can be successfully prepared by CHPACl and ammonia modification. Additionally, to further confirm the modification reactions, zeta potential measurements of bare and modified p(TA) particles in 0.001 M KCl solution were carried out and are summarized in Table 1. The value of zeta potential of bare p(TA) particles, and CHPACl and NH_3 modified p(TA) particles were found as -27±1, -18±3, and -13±4 mV, respectively. These results show that modified particles possess some positive charges on the network of p(TA) and their zeta potentials increased or shifted toward more positive values in comparison to unmodified p(TA) particles.

The modified p(TA) particles can be used as template for in situ metal nanoparticle preparation after loading metal salts, such as $CoCl_2$, $NiCl_2$, and $CuCl_2$ in ethyl alcohol, into the microgels. As presented in Figure 3a, modified p(TA) particles were laden with metal salts ($CoCl_2$, $NiCl_2$, $CuCl_2$) in ethyl alcohol to form IL colloids because of the electrostatic interaction between metal salts and charged groups on p(TA). It is reported that TA molecules have strong affinity for metal ions due to the -OH groups on phenol groups in the TA structure. Das and Velusamy determined that phenolic compounds such as hydroxyl and ketonic groups are able to bind to metal ions because of the nucleophilic character of the aromatic ring in the molecular structure.[46] Flavonoids such as TA are also known for effective scavenging properties for reactive oxygen species. It was reported that metal nanoparticles formation mechanism in modified p(TA) particle network is facilitated due to complex formation between the metal ions and -O$^-$ groups in TA molecules to their corresponding zero valent forms.[47] Therefore, the colors of metal salt-loaded particles were different from the p(TA) particles without metal ions, and are darker as an indication of particle formation. In addition to the reduction ability of TA molecules, the metal salt-containing p(TA) particles were exposed to $NaBH_4$ solution for complete reduction of the metal chlorides to the corresponding metal nanoparticles. The color of in situ metal nanoparticle-containing composite ILs p(TA)-M particles turned to an even darker black color as illustrated in the bottom right of Figure 3a. The TEM images of the metal nanoparticles within p(TA)-M IL composites are shown in Figure 3b. As can be seen from TEM images; Co, Ni or Cu nanoparticles are spherical in shape with the sizes ranging from about 5 nm to few of tens of nanometer.

The thermal stability of modified p(TA) and metal-loaded ILs composite of p(TA)-M particles are illustrated in Figure 4. The onset thermal degradation of the p(TA) modified with ammonia started at about 75 °C and continued up to 140 °C with slight degradation of about 1.3% weight, most probably due to the loss of bound water. The main thermal degradation range was observed between 210 to 496 °C with 76.1 wt % loss. The degradation of p(TA) particles modified with CHPACl was similar to p(TA) particles treated with ammonia. The metal salt-loaded composite thermograms also exhibited similar thermal degradation profile to the modified p(TA) particles. Heating up to 993 °C, modified p(TA) particles and the ILs composite of p(TA)-$[CuCl_4]^{-2}$, p(TA)-$[NiCl_4]^{-2}$ and p(TA)-$[CoCl_4]^{-2}$ particles displayed 85.4% 75.6%, 73.4% and 72.9% weight loss, respectively. The TGA results show that addition of metal salts increases the thermal stability of p(TA) particles. The metal contents of the IL composite particles of p(TA)-M were estimated at 9.7 wt.% Cu, 11.9 wt.% Ni, and 12.4 wt.% Co in comparison to modified p(TA) particles as given in Table 2. In order to determine the exact amount of metals in composite ILs p(TA) particles, the metal nanoparticles were treated with 10 ml 1 M HCl for 24 h, and the metal ion concentration was measured by AAS. According to the AAS results given in Table 2, 1 g IL composite of p(TA)-M particles contains 45.8±5 mg Co, 36.5±3 mg Ni and 25.1±2 mg Cu ions, whereas, unmodified p(TA)-M composite particles have 40.0±3 mg Co, 35.5±0 mg Ni and 27.1±1 mg Cu ions.

3.2. Catalytic activity of p(TA)-M ILs composite particles

Nitro aromatic compounds and dyes are present in most surface and ground waters, and are also identified as toxic pollutant materials, as they are discharged or effluents from many industrial wastewater streams from textile, paper, plastic, leather and pharmaceutical industries,[40] and some of these compounds are recognized as carcinogens. One of the toxic compounds, 4-NP, can be reduced to 4-AP which is non toxic and a useful material for several pharmaceutical applications. Metal nanoparticles and metal alloys of Co, Ni, Cu, Fe, Pd, Pt, Au, and Ag nanoparticles have been reported as catalyst for diverse reactions including nitro compounds and various dye reductions with high catalytic activity.[41-43] The materials prepared here as green or environmentally-friendly IL composites of p(TA)-M particles were shown to be very useful catalysts in the reduction of toxic organic compounds, such as 4-NP and dyes e.g., MB and EY.

3.2.1. Catalytic degradation of 4-NP to 4-AP by p(TA)-M

The catalytic reduction scheme of 4-NP, and its corresponding UV-Vis spectrum of the conversion of 4-NP to 4-AP catalyzed by p(TA)-Co composite ILs containing 0.059 mmol Co nanoparticles in the presence of $NaBH_4$ at 30 °C, are illustrated in Figure 5a and 5b, respectively. As shown in the UV-Vis spectrum, the peak at 400 nm, assumed to be the 4-nitrophenolate anion due to existence of $NaBH_4$ alkaline solution, decreased whereas the 4-AP peak at 290 nm increased. To investigated the modification effects on the catalytic activity of the catalysts system, unmodified p(TA)-Cu and modified p(TA)-Cu composite ILs containing the same amount of catalyst e.g., 0.059 mmol Cu nanoparticles, were used in the reduction of 4-NP and their results are shown in the Figure 5c. The rate constants (*k*) of unmodified and modified composite p(TA)-Cu ILc particles with CHPACl and ammonia were found as 0.72, 0.58, 0.92 min^{-1} in 4-NP reduction, respectively. Therefore, ammonia modified p(TA)-Cu composite ILC particles have the best catalytic performances in comparison to the unmodified and modified p(TA)-Cu forms. The chemical structure of catalyst systems also play significant role by aiding electron transfer from electron donor $NaBH_4$ to accepted nitro compounds.[48] Therefore, effectively catalyst systems such as ammonia modified p(TA)-Cu composite can increase the transfer of electron acting as an electron relay system in the reduction on nitro compounds due to their highly ionic nature within the polymer network due to the natural ILC structure. Thus, all the other experiment were done with modified p(TA)-M ILc particles with ammonia for catalyst reactions. As Co, Ni and Cu nanoparticles are widely used as catalysts in the reduction of nitrophenol,[23,36,37,39,42,46,49] to determine the catalytic activity of same amount of Co, Ni, and Cu nanoparticle-containing p(TA)-M, composite ILs and bare p(TA) particles were used in the reduction of 4-NP under the same reaction conditions and the corresponding graphs are illustrated in Figure 5d and 5e. In Figure 5d, the metal nanoparticles were obtained by self reduction of TA molecules in p(TA), whereas in Figure. 5e, the metal nanoparticles were prepared by $NaBH_4$ treatment of the metal salts loaded within p(TA). It is interesting that self-reduction of metal nanoparticles by TA molecules seemed to generate better catalytic performances. For Figure 5d, the 4-NP reduction rate constants (*k*) were calculated as 0.41, 0.45, 0.92 min^{-1} for Co, Ni, and Cu composites, respectively. It is obvious that Cu nanoparticles provided the best catalytic activity compared with Co and Ni nanoparticle-containing p(TA) composites. The reduction rate of p(TA)-Co and p(TA)-Ni composite ILs particles were found to have almost the same reduction rate. In the literature, many metal and alloy catalysts have been used for the 4-NP reduction. Butun and Sahiner studied the catalytic performance of different metal nanoparticles and reported that Co and Ni have the same catalytic performance but Ag and Cu nanoparticles have better catalytic performances.[46] According to previous studies, in situ metal nanoparticles prepared in polymer matrices require the presence of $NaBH_4$.[50] On the other hand, TA molecules are known to reduce most of the metal ions to the corresponding salts due to abundant number of -OH and phenol groups in their molecular structure.[46,47] Therefore, here catalytic performances of p(TA)-M particles prepared with and without $NaBH_4$ were used in 4-NP reduction and their catalytic performances were compared (Figure 5d and 5e). The rate constant value for 4-NP reduction catalyzed by p(TA)-Cu composite ILs prepared without and with the use of $NaBH_4$ were calculated as 0.92 and 0.82 min^{-1}, respectively, under the same experimental conditions. Therefore, reducing metal salts with $NaBH_4$ within the p(TA) particle matrices decreased the catalytic activity of particles, most probably due to formation of some boron-containing metal nanoparticles.[22,23]

As 4-NP reduction by the p(TA)-Cu composites is very fast, we investigated the effect of temperature on the reduction of 4-NP catalyzed by p(TA)-Co particles at five different temperatures (30, 40, 50, 60, and 70 °C) under the same reaction conditions. Figure 6a demonstrates the decrease in the concentration of 4-NP with time at different temperatures. The reduction rate constants (*k*) values are given in Table 3. As can be clearly seen from the results, the reduction rate constant of the reaction increased with increasing temperature, and the 4-NP reduction rate is found to follow pseudo first order reaction kinetics because of a linear correlation of the natural logarithmic of concentration decease with time, as shown in Figure 6b. The activation energy of 4-NP reactions at five different temperatures were calculated using the Arrhenius equation (Eq. (1))

$$\ln k = \ln A - (E_a/RT) \qquad (1)$$

Where, E_a is activation energy, A is Arrhenius factor, T is temperature and R is the ideal gas constant (8.314 JK^{-1} mol^{-1}). The activation energy values were 26.19 kJ mol^{-1} from the plot of ln k vs. 1/T as shown in Figure 6c and Table 3. The kinetic parameters such as activation enthalpy ($\Delta H^{\#}$) and activation entropy ($\Delta S^{\#}$) were calculated using the Eyring equation (Eq. (2)).

$$\ln (k/T) = \ln (k_B/h) + \Delta S^{\#}/R - \Delta H^{\#}/R\ (1/T) \qquad (2)$$

Where, k_B is the Boltzmann constant (1.381 x 10^{-23} JK^{-1}) and h is the Planck constant (6.626 x 10^{-34} JK^{-1} mol^{-1}). Figure 6d illustrates the graphs of ln(k/T) against 1/T for the 4-NP reduction calculated for different temperatures. The values of enthalpy and entropy for the 4-NP reaction catalyzed by p(TA)-Co ILs composite were calculated as 23.12 $kJmol^{-1}$, and -182.35 $Jmol^{-1}K^{-1}$, respectively, as given in Table 3. Earlier studies reported that the E_a values for p(AAGA)-Ag and p(SPM)-Cu hydrogel composite catalyst systems were 33.8 and 33.86 $kJmol^{-1}$, respectively.[49,51] Furthermore, the total turnover frequency (TOF) of the 4-NP reduction by p(TA)-Co composite ILs were calculated as 1.12, 1.41, 1.88, 2.42, and 3.38 mol 4-NP (mol $Co.min)^{-1}$ for the reaction temperatures 30, 40, 50, 60, and 70 °C, respectively. The total TOF values of 0.213 mol 4-NP (mol $Co.min)^{-1}$ for p(AMPS)-Co hydrogel catalysts was also reported in the literature.[42] TOF values are calculated based on the number of moles of reduced 4-NP per mol of catalyst per unit time. Therefore, the p(TA)-Co composite ILs provided better catalytic performances in comparison to similar catalytic systems for the 4-NP reduction reaction.[42,49,51]

The reusability of catalyst is an important subject to determine the faith of catalyst in true industrial applications. Therefore, the p(TA)-Cu composite ILs particles was used in the same 4-NP reduction repetitively five time in one day, and their % activity of catalyst system was determined and graphed in Figure 7. The % catalytic activity was calculated based on the % ratio of reduction rates after each use to the first use. It is obvious that the catalytic activity of p(TA)-Cu composite ILs particles is the same after 2nd usage, but then the catalytic activity was found decrease to 83% at the end of the 5th use. Therefore, p(TA)-Cu composite IL particles has great potential in real industrial applications.

3.2.2. Catalytic reduction of methylene blue by p(TA)-Cu ILs composite

MB is a heterocyclic aromatic dye, shown in Figure 8a, which can be reduced to leucomethylene blue (LMB) in the presence of $NaBH_4$ but the reduction rate is very slow.[46] Therefore, metal nanoparticle-containing p(TA)-M ILs composites can be used to accelerate the reduction rate of MB, and such a reduction can be monitored by UV-Vis spectroscopy. Therefore, the MB decolonization/reduction was carried out by p(TA)-Cu ILs composite (containing 0.0039 mmol Cu nanoparticles) in the presence of 2x10^{-2} M $NaBH_4$ at 800 rpm rate, and the corresponding change in absorption maxima with time of the UV–Vis spectra is given in Figure 8b. The maximum absorption band of MB appears at 664 nm, as can be seen this MB absorption band was completely reduced within 3 min by p(TA)-Cu ILs composite at room temperature. In Figure 8c, reduction rate constants (*k*) for MB were calculated as 0.95, 0.077, 0.02, and 0.007 min^{-1} for Cu, Co, and Ni composites, and bare p(TA) particles, respectively. For control, only 2x10^{-2} M $NaBH_4$ containing medium with bare p(TA) (no metal catalyst) was used, and found that the MB solution reduced very slowly with 0.007 min^{-1} rate constant but it was not completely reduced in the course of reaction time (2h). The catalytic activity of p(TA)-M composite particles in order to Cu>Co>Ni were observed. This toxic compound can be found in a variety of wastes and different contaminated water sources, such as fresh waters of rivers and lakes, seawater, or even drinking waters such as tap waters. Therefore, the removal of organic contaminants by adsorption or degradation from these different water sources has paramount significance, and depends on different medium conditions such as pH, ionic strength, temperature, and so on. For this reason, MB degradation/decolorization catalyzed by p(TA)-Cu ILs composite was investigated in different water media, under the same reaction conditions. Figure 8d shows the reduction of MB solution prepared in different media, DI water, tap water, fresh water (creek water), and sea water, catalyzed by p(TA)-Cu ILs composite at room temperature. The pH and conductivity values of MB were given in Table 4. As can be seen, the pH and conductivity values are changed significantly depending on the medium and increased in the order of DI water < tap water < Saricay water < seawater. Especially, the pH and conductivity of seawater containing MB was measured as 8.40±0.09 and 439.2±7 μs cm^{-1}, whereas, the same values of DI was measured as 6.15±0.04, and 0.61±0.1 μs cm^{-1}. As demonstrated in Figure 8d, the reduction reaction of MB to LMB in sea water and Saricay water (creek water) were catalyzed by p(TA)-Cu composite ILs faster than the reduction rates in DI water and tap water under the same reaction conditions. It is interesting that the salty environment (high ionic strength) enhanced the catalytic reduction rate of MB in comparison to tap and DI water. The existence of other solutes in creek water also increases the reduction rates. Consequently, it can be said that the environmentally benign and green microgel composite works even in natural environments making it better for real applications e.g., reduction of organic dyes and contaminates.

3.2.3. Catalytic reduction of eosin Y by p(TA)-Cu ILs composite

Another dye, EY, anionic in character compared to MB as shown in Figure 9a, was also used in the reduction experiment catalyzed by p(TA)-Cu ILs composite. The characteristic absorption peak of eosin Y, a tetrabromoflourescein dye, appears at 514 nm and earlier studies indicated that the reduction rate of EY is very slow in the absence of a catalyst.[51] As illustrated in Figure 9b, EY reduction in 100 mL $8x10^{-4}$ DI water reduction catalyzed by p(TA)–Cu ILs composite containing 0.0039 mmol Cu nanoparticles in the presence of $2x10^{-2}$ M $NaBH_4$ was completed, and absorption maxima with time clearly show the decrease in absorbance was completed within 10 min. To investigated the effects of metal species on EY reduction, Co, Ni, Cu catalyst containing p(TA)-M composite and bare p(TA) particles catalytic performances were compared in EY reduction in presence of $2x10^{-2}$ M $NaBH_4$ shown in Figure 9c. From the figure, Cu catalyst has the best catalytic performance with 0.2 min^{-1} rate constant for EY reduction, and it was found that Co and Ni catalyst composite particles that are provided 0.07, 0.05 min^{-1} rate constants. And the non catalyst system (control, just bare p(TA)) provided 0.04 min^{-1} rate constants. Again, to determine the effects of medium on EY reduction, different EY solutions in various aquatic media such as DI water, tap water, fresh water (Saricay creek) and seawater were prepared, and their reduction catalyzed by p(TA)–Cu ILs composites were investigated under the same reaction conditions. The decrease in the initial concentration of EY with time in different aqueous media is shown in Figure 9d. As can be seen, the EY reduction was finished within 5 min in seawater and creek water; however, the reduction was completed within 10 min for DI water. Again, results for EY reduction in sea and fresh water (creek water) provided better environments for the catalytic reduction of EY catalyzed by p(TA)-Cu ILs composite. To understand the fast reduction of EY in seawater, a control experiments was carried out e.g., without any catalyst system and microgel just using seawater and EY, and as demonstrated in Figure 9d, seawater able to finish EY reduction within 18 min. This could be due to the existence of high ionic nature or higher saltiness of these media in comparison to DI and tap waters. These results further corroborate that the high ionic solution medium cause an increase in the reduction of EY due to the accelerating effect of electron transfer mechanism[48]. Again, as shown in Table 4, the pH values of EY solution in DI water, tap water, Saricay water, and seawater was measured as 5.5, 7.6, 8.36, 7.95, and the corresponding conductivities were measured as 0.44, 5.87, 202.6, 483 µs cm^{-1}, respectively confirming the lineer relation between the ionic strenght of the medium and the reaction rates. The kinetic data of MB and EY reductions in different aqueous media catalyzed by p(TA)-Cu ILs composite containing 0.0039 mmol Cu nanoparticles in the presence of $2x10^{-2}$ M $NaBH_4$ are shown in Table 5. As can be seen the results indicate that the reaction rate constants (*k*) in seawater for both dyes were found to be higher than the rate constants in the other media. Furthermore, the total TOF for MB and EY reduction in different media catalyzed by p(TA)-Cu ILs composite was calculated. The TOF values in DI water reactions were 2.74 mol MB mol $catalyst^{-1}$ min^{-1} and 1.85 mol EY mol $catalyst^{-1}$ min^{-1}, whereas the TOF values for seawater reactions were 4.10 mol MB mol $catalyst^{-1}$ min^{-1} and 3.74 mol EY mol $catalyst^{-1}$ min^{-1}. Therefore, for the reduction of EY and MB dyes, the p(TA)-Cu ILs composite performed better in media that are most likely to be contaminated. As a result, p(TA)-Cu ILs composite can be used to clean organic dye- or nitro compound-contaminated natural waters.

To investigated the thermodynamic parameters for MB and EY reductions, the reaction rate constants (k), TOF (mol MB or EY mol $catalyst^{-1}min^{-1}$) values, activation energy (E_a), enthalpy (ΔH) and entropies (ΔS) were calculated catalyzed by p(TA)-Cu composite IL particles for the reaction carried out at five different temperatures: 30, 40, 50, 60, and 70 °C, under the same reaction conditions, and the results are summarized in Table 3. The reduction rate constants (*k*) values for MB and EY reactions were calculated as 0.68 and 0.30 min^{-1} at 30°C, whereas, rate constant (*k*) values were increased to 4.12 and 0.84 min^{-1} for MB and EY reactions at 70 °C. Moreover, the TOF values for MB and EY reductions catalyzed by p(TA)-Cu were increased to 23.44 mol MB mol $catalyst^{-1}$ min^{-1} and 16.41 mol EY mol $catalyst^{-1}$ min^{-1} at 70 °C from 3.28 MB mol $catalyst^{-1}$ min^{-1},and 2.93 mol EY mol $catalyst^{-1}$ min^{-1} at 30 °C. From Table 3, rate constants and TOF values were increased with increasing temperature. The activation energy, enthalpy, and entropy were calculated as 38.89 kJ mol^{-1}, 35.43 kJ mol^{-1}, and -127.54 J mol^{-1} K^{-1}, respectively, for the reduction of MB dye. These values for EY reduction catalyzed by p(TA)-Cu composite ILC particles were found as 22.88 kJ mol^{-1} for Ea, 19.76 kJ mol^{-1} for ΔH, and –188.31 J mol^{-1} K^{-1} for ΔS, respectively. Therefore, it can be presume that, EY reduction reaction by the p(TA)-Cu catalyst is resulted in better catalytic activity than MB reduction with the same catalyst. Gupta et al. reported that the activation energy of MB reduction with gold catalyst was found to be about 38.42 kJ mol^{-1}.[53] Moreover, Srivastava et al. demonstrated that the activation energy of EY reduction catalyzed by gold nanorod was determined as 32.84 kJ mol^{-1}.[54] Therefore, this current research that employed p(TA)-Cu catalyst system provided better catalytic performances on MB and EY reductions in comparison to the similar studies in the literature.[53, 54]

4. Conclusions

Herein, a simple synthesis of p(TA) particles in a single step is reported by using epoxy-based cross linker, TMPGDE, with a high yield (73±6%). These prepared natural particles were found to be very useful for in situ metal nanoparticle preparation due to the self-reducing ability of TA molecules for different metal ions such as Cu, Co, and Ni. P(TA) microgels were modified by chemical treatments to form ILs.

To sum up;

-P(TA) particles can be modified with 3-chloro-2-hydroxypropyl ammonium chloride and ammonia aqueous solution to generate positive charges on p(TA), and neutralized with NH_3 to form ammonium salt of p(TA) as natural ionic liquid polymeric particles.

-The modified p(TA) particles can be used for in situ metal nanoparticle preparation after loading metal salts such as $CoCl_2$, $NiCl_2$ and $CuCl_2$ in ethyl alcohol into NH_3-modified p(TA) ILCs.

-It was found that without $NaBH_4$ treatments of the metal salt-laden p(TA) particles, TA molecules reduce the metal salts to the corresponding metal nanoparticles readily, and provide better catalytic performances in the catalytic reduction of nitro compounds and organic dyes.

-Kinetic parameters such as energy, enthalpy and entropy of the 4-NP reduction catalyzed by p(TA)-Co composites were calculated as 26.19 kJmol^{-1} for Ea, 23.12 kJmol^{-1} for ΔH and -182.35 Jmol^{-1}K^{-1} for ΔS, respectively.

-The reduction of toxic organic compounds in addition to 4-nitrophenol, such as EY and MB, catalyzed by p(TA)-M IL composite were shown to be very efficient. In addition, interestingly, it was found that MB and EY reduction in natural waters such as seawater and creek waters was much faster than the reduction reactions in DI and tap waters, suggesting the great potential for the real application of p(TA)-M IL composite to clean organic nitro compound- or dye-contaminated waters.

The conclusions section should come at the end of article.

Acknowledgments

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Notes and references

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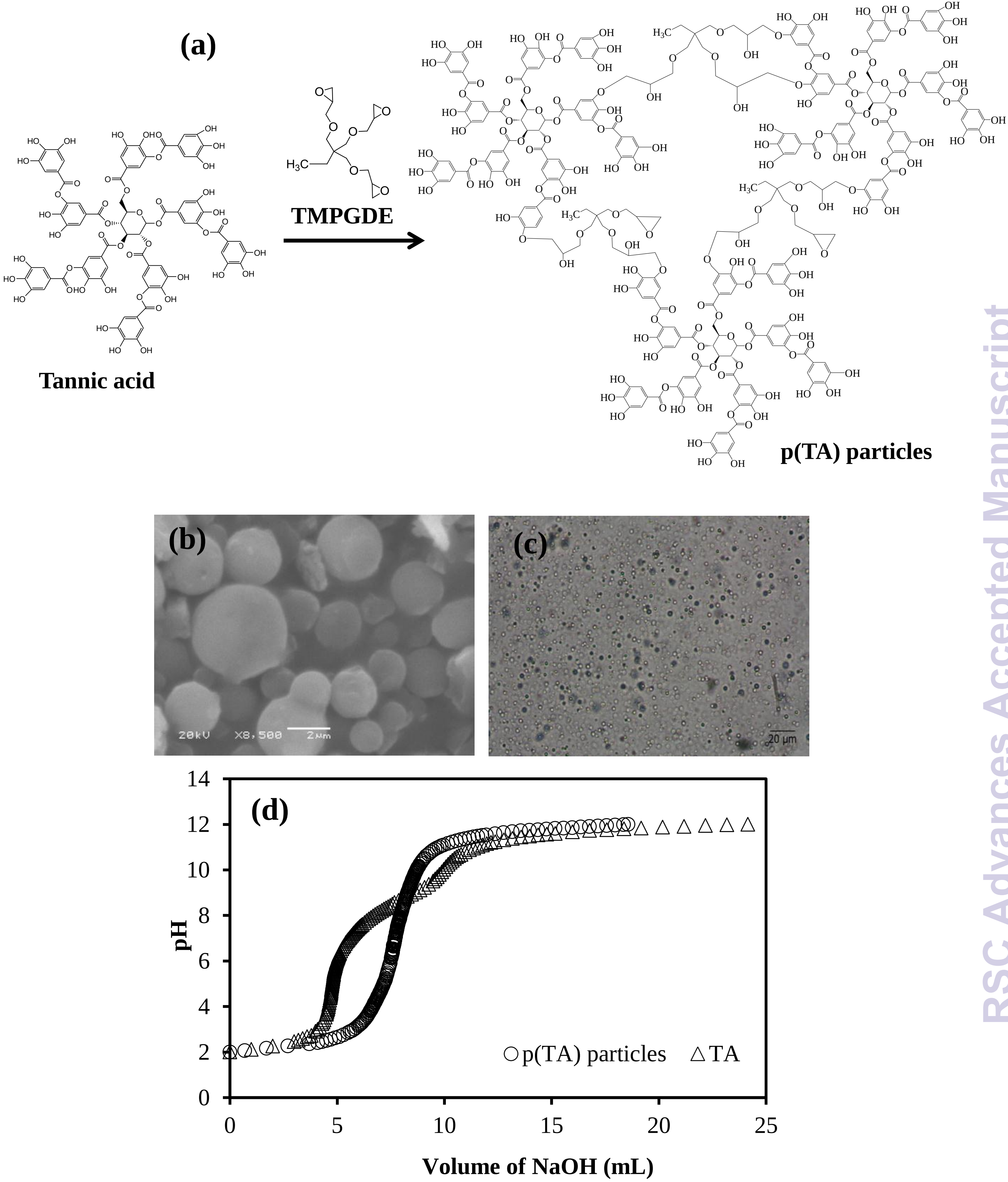

Fig. 1. (a) Schematic representation of synthesis of p(TA) particles, **(b)** SEM, and **(c)** optic microscope images of p(TA) particle, **(d)** potentiometric titration profile of TA and p(TA) particles at ionic strength of 0.01 M 50 ml KCl solution with 0.1 M NaOH.

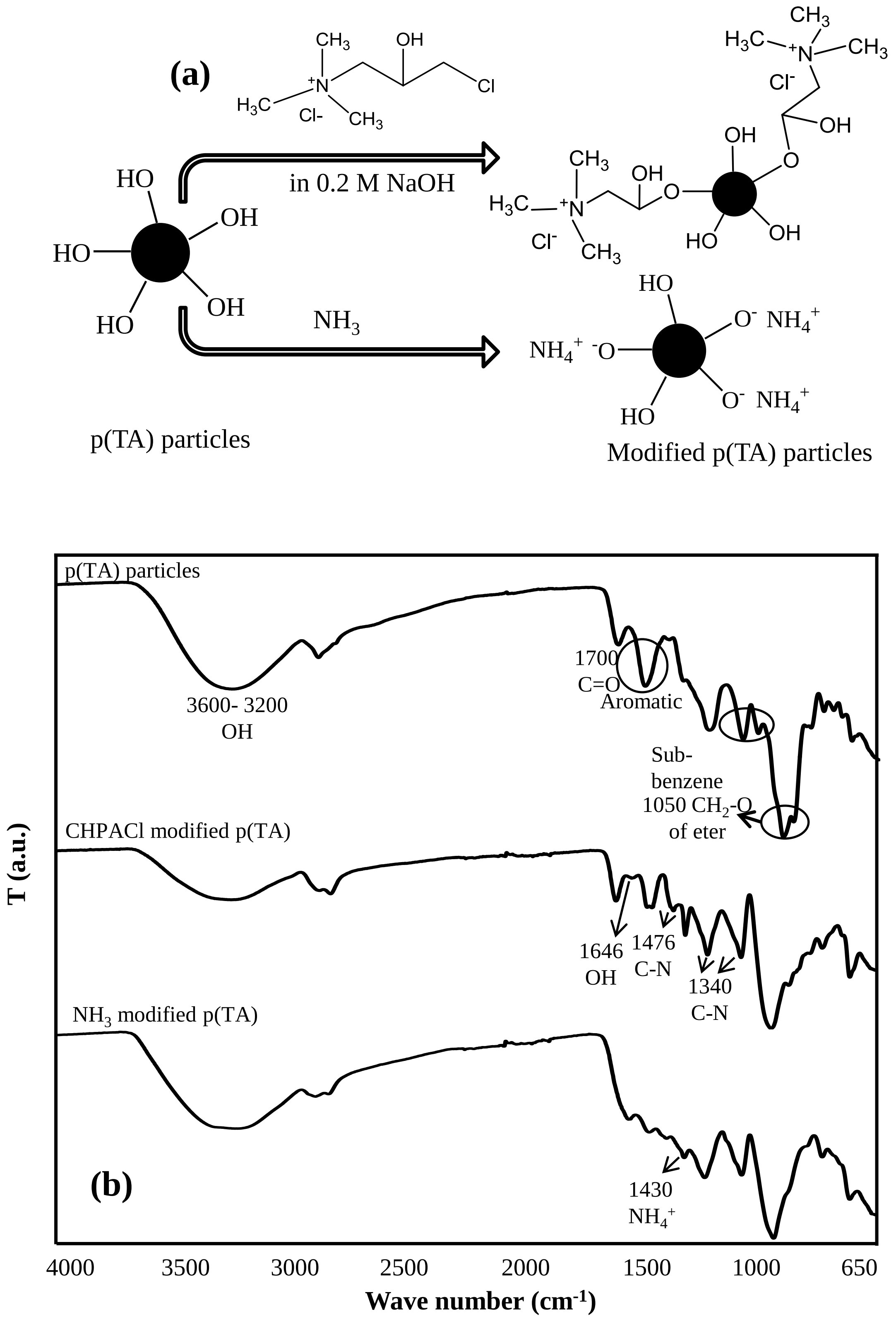

Fig. 2. (a) The schematic representation of the modification mechanism of p(TA) particles, and **(b)** FT-IR spectra of p(TA) and modified p(TA) particles.

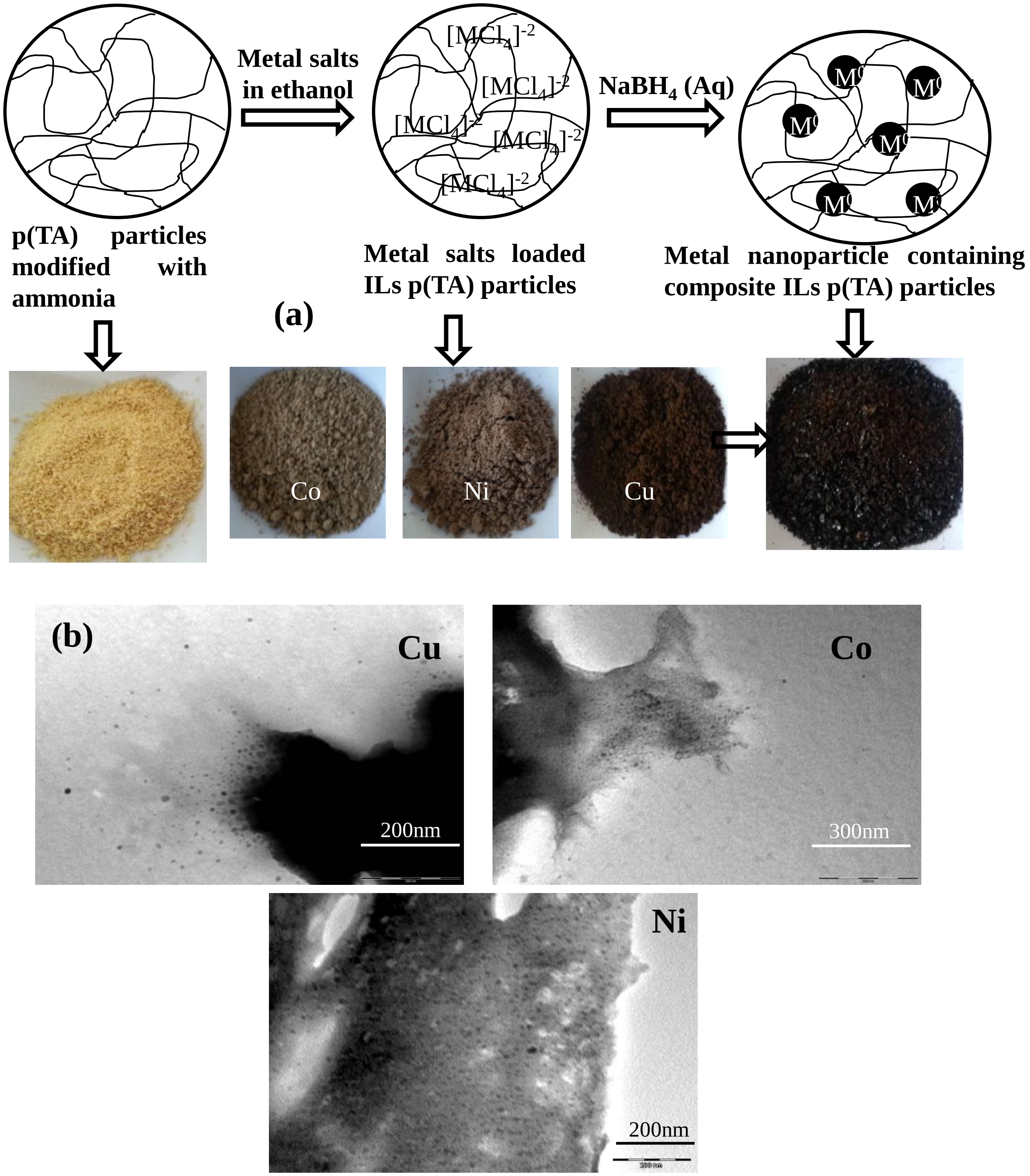

Fig. 3. (a) Schematic presentation of metal chloride absorption by p(TA) particles, and their reduction to corresponding metal nanoparticles. **(b)** The TEM images of metal nanoparticle within p(TA)-M composites.

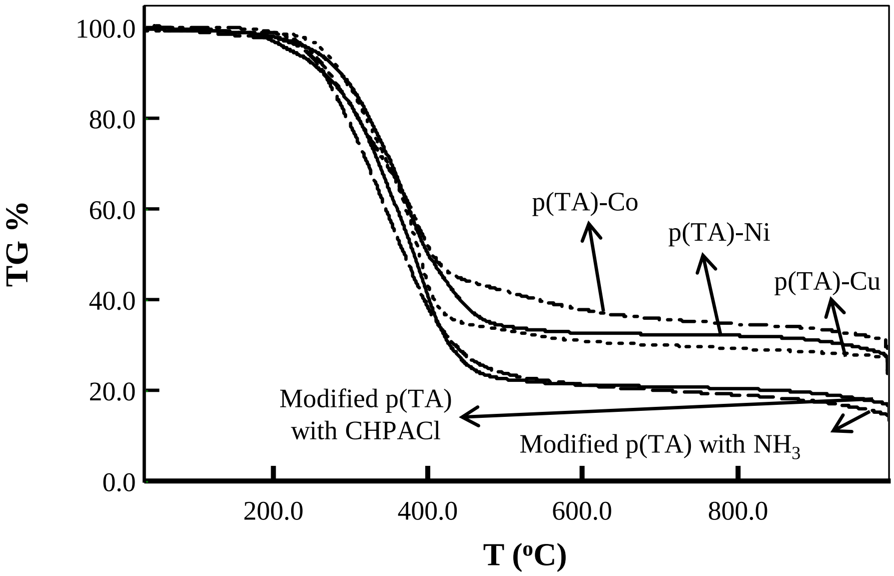

Fig. 4. TGA thermograms of p(TA) particles modified with CHPACl, and with ammonia and modified composites containing metal nanoparticles (Co, Ni, Cu) (p(TA)-M particles prepared after modification with NH_3 with ammonia) [M: 9.7 wt % of Cu, 11.9 wt of % Ni, 12.4 wt % of Co].

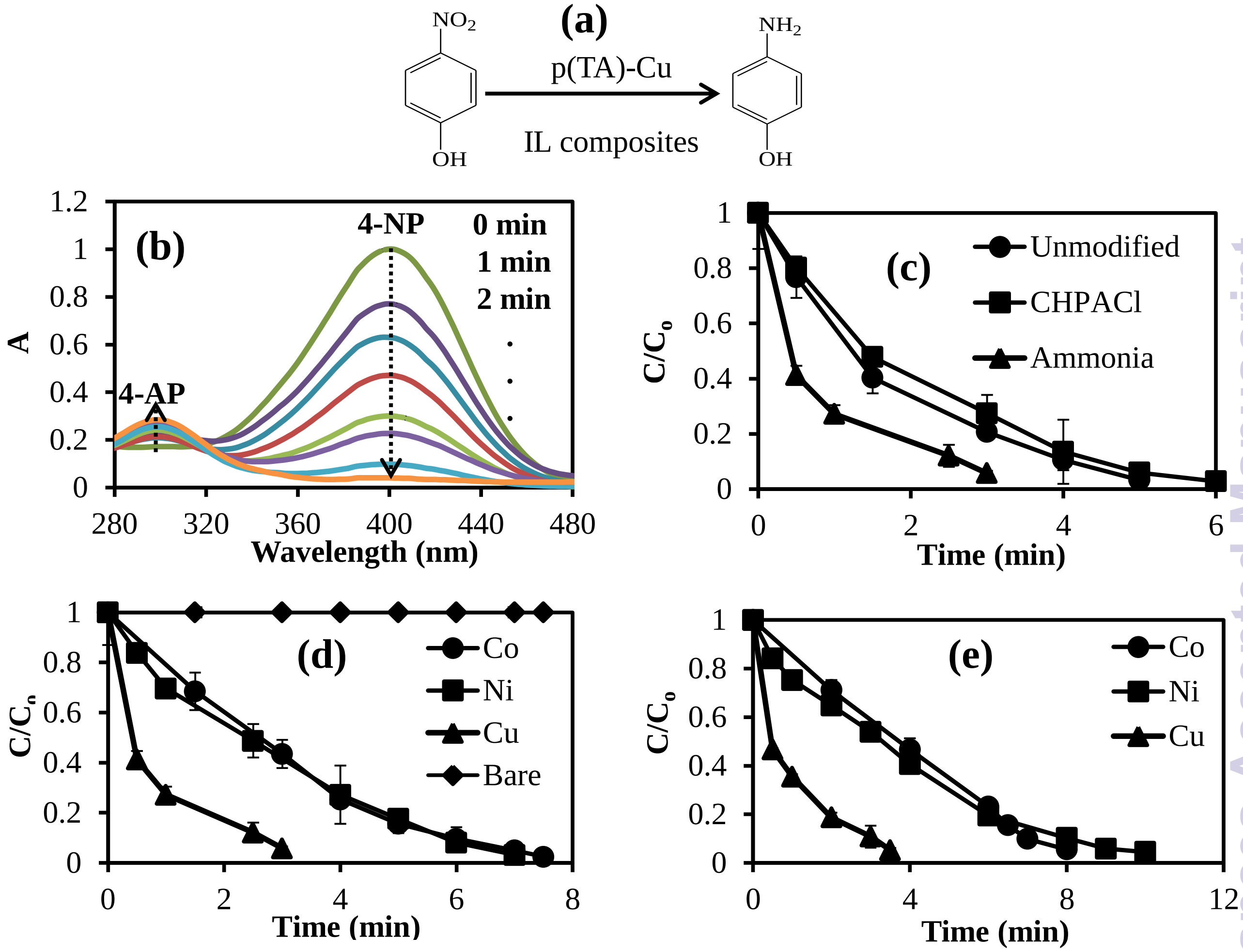

Fig. 5. (a) The schema of 4-NP reduction to 4-AP catalyzed by p(TA)–M composite particles. **(b)** UV–Vis spectra of the reduction of 4-NP to 4-AP by p(TA)–Co IL composite particles (containing 0.059 mmol Co nanoparticles). **(c)** The 4-NP reduction rates by unmodified p(TA)-Cu, and modified p(TA)-Cu with CHPACl and NH_3 IL composite particles (containing 0.059 mmol Cu nanoparticles). The 4-NP reduction rates by **(d)** bare and p(TA)–M composites (M: Cu, Ni, Co) and M obtained by self reduction of TA without $NaBH_4$ treatment, and **(e)** p(TA)-M composite with M obtained by $NaBH_4$ treatment [M: Co, Ni, and Cu each 0.059 mmol; 50 mL 4-NP solution containing 0.01 M 4-NP and 0.4 M $NaBH_4$ at 30 °C, 800 rpm].

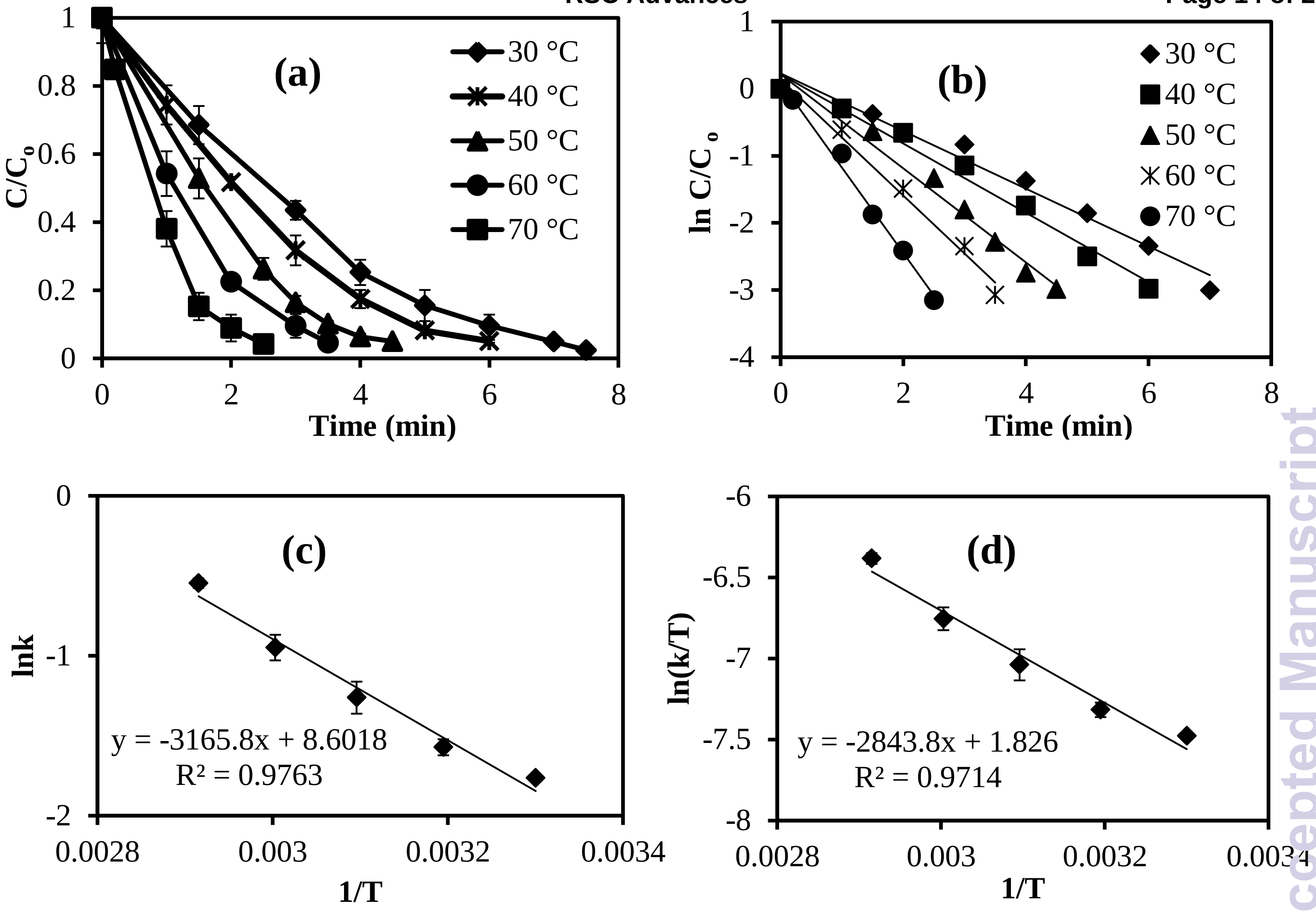

Fig. 6. (a) The change in the concentration of 4-NP with time during the 4-NP reduction reaction by p(TA)-Co composite ILs catalyst, **(b)** ln C/C$_o$ vs. time of the same graph, and **(c)** ln k 1/T graphs (Arrhenius equation), and **(d)** ln (k/T) vs. 1/T graphs (Eyring equation) [Reaction conditions: composite ILs p(TA)-Co particle containing 0.059 mmol Co, 50 mL 4-NP solution containing 0.01 M 4-NP and 0.4 M NaBH$_4$, at 800 rpm].

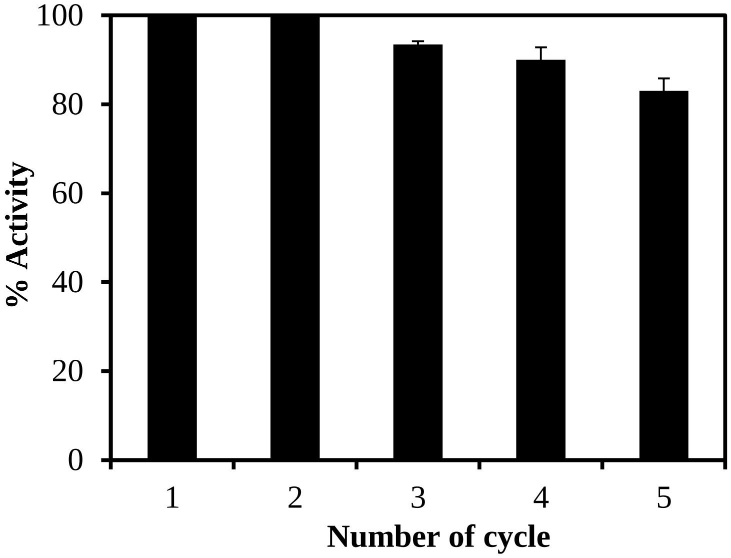

Fig. 7. The reusability of p(TA)-Cu composite IL particles for 4-NP reaction under the same reaction conditions. [Reaction conditions: composite ILs p(TA)-Co particle containing 0.059 mmol Cu, 50 mL 4-NP solution containing 0.01 M 4-NP and 0.4 M $NaBH_4$, at 800 rpm].

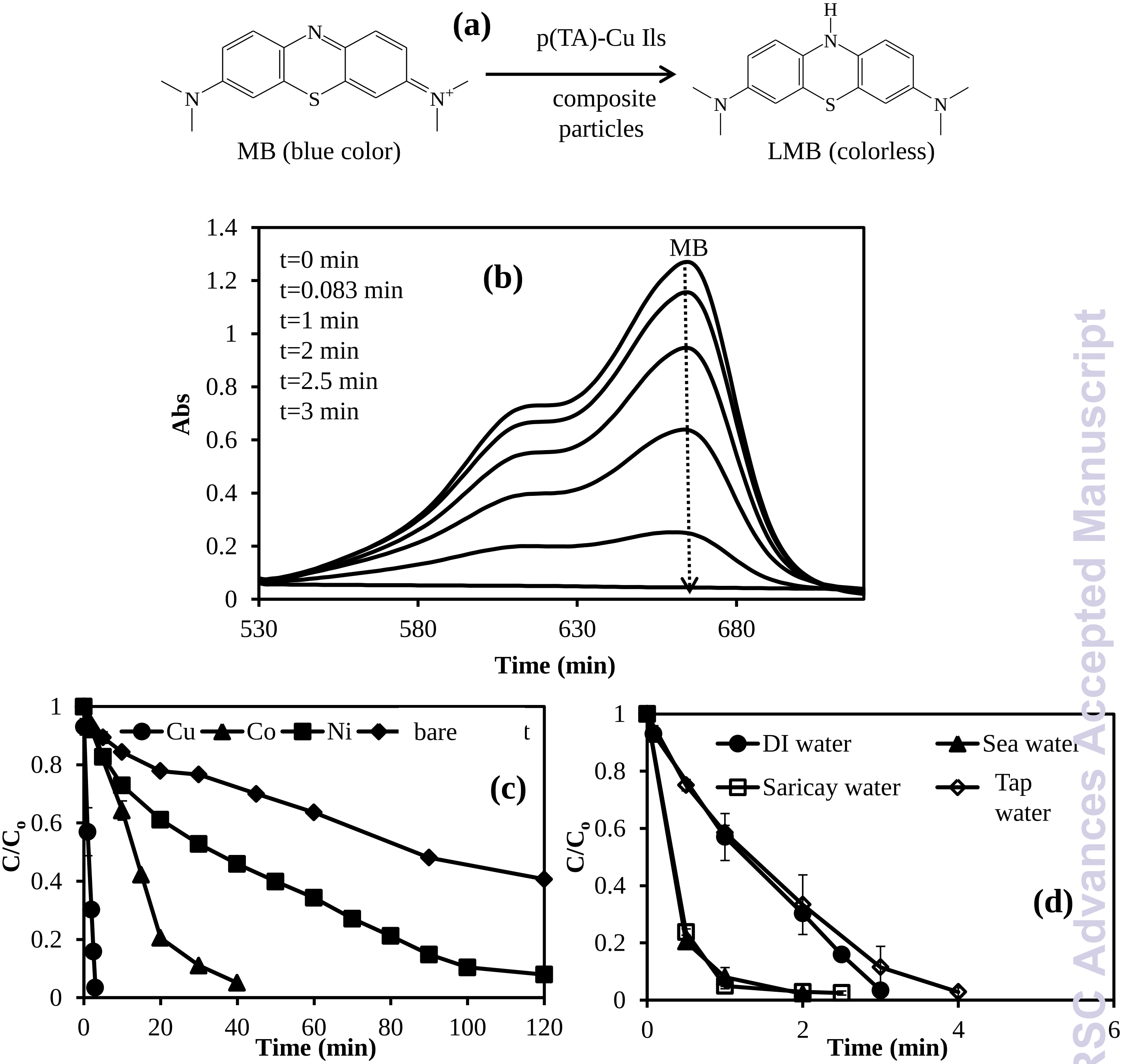

Fig. 8. (a) The schema of methylene blue (MB) reduction reaction to leucomethylene blue (LMB) catalyzed by p(TA)–Cu ILs composite. **(b)** UV–Vis spectra of the reduction of MB catalyzed by p(TA)–Cu ILs composite, containing 0.0039 mmol Cu nanoparticles. (c) The reduction rates of MB by p(TA)-M composite particles [M: Co, Ni, and Cu and 0.0039 mmol each; 100 mL 3.2x10^{-4} M MB, and 2x10^{-2} M $NaBH_4$ at 800 rpm]. **(d)** The reduction rates of MB in different aquatic environments [reaction conditions: ILs composite p(TA)–Cu particles containing 0.0039 mmol Cu, 100 mL 3.2x10^{-4} M MB, and 2x10^{-2} M $NaBH_4$ at 800 rpm].

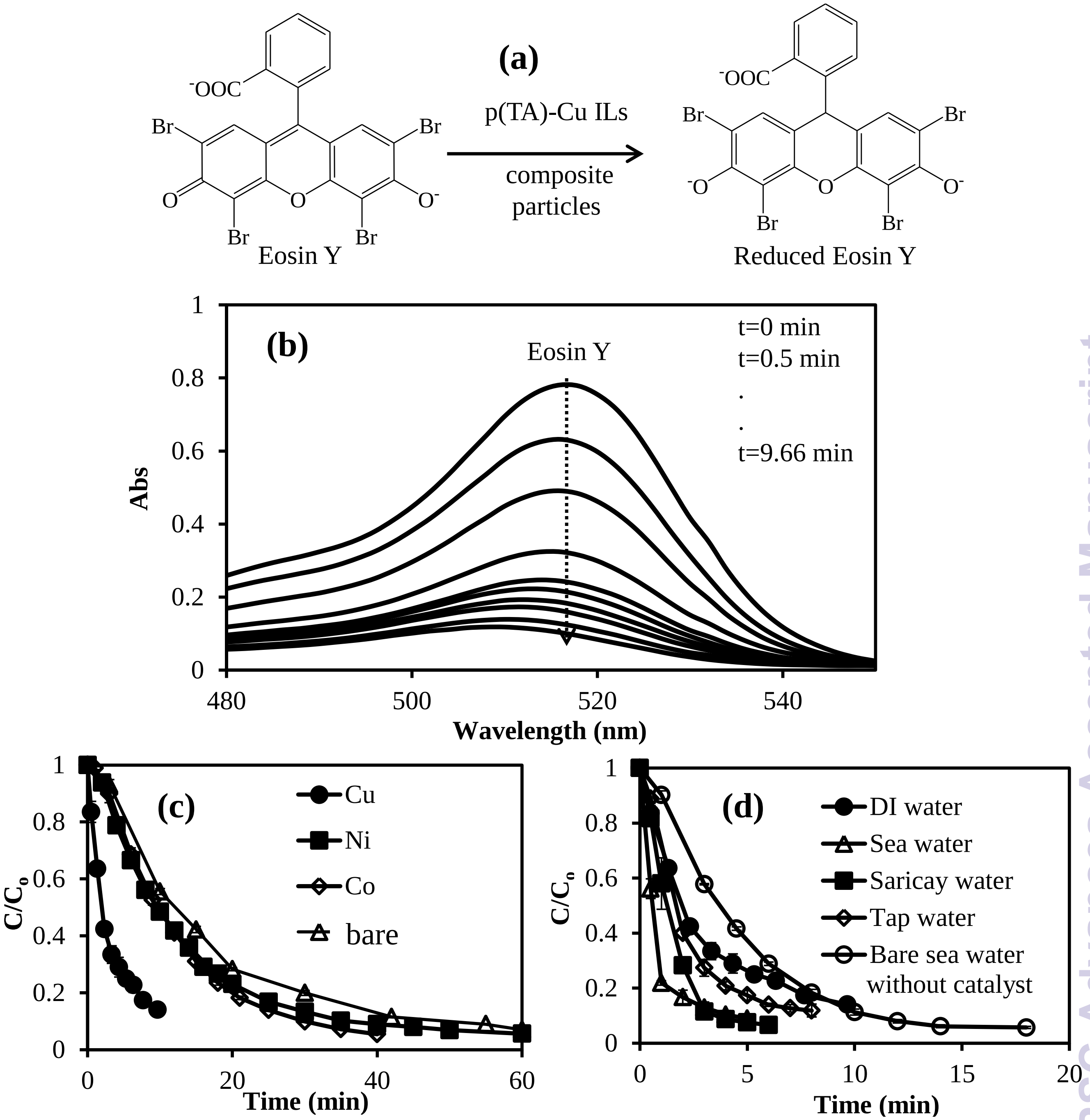

Fig. 9. (a) The schema of eosin Y (EY) reduction reaction catalyzed by p(TA)-Cu ILs composite. **(b)** UV–Vis absorption spectra of EY reduction with time catalyzed by p(TA)-Cu ILs composite (containing 0.0039 mmol Cu nanoparticles). **(c)** The reduction rates of EY by p(TA)-M composites particles [M: Co, Ni, and Cu and 0.0039 mmol each; 100 mL EY solution, $8x10^{-4}$ M and $2x10^{-2}$ M $NaBH_4$ at 800 rpm]. **(d)** The reduction rates of EY solution in different aqueous media [Reaction conditions: p(TA)–Cu particles containing 0.0039 mmol Cu, 100 mL eosin Y solution, $8x10^{-4}$ M and $2x10^{-2}$ M $NaBH_4$ at 800 rpm].

Table 1. Zeta potentials of p(TA), and modified p(TA) particles in 0.001 M KCl aqueous solution at pH 5.5.

Materials	**Zeta potential (mV)**
P(TA) particles	-27 ±1
Modified p(TA) particles with CHPACl	-18 ±3
Modified p(TA) particles with ammonia	-13 ±4

Table 2. The amount of metal ions inside the unmodified p(TA), modified p(TA)-M composite ILs particles.

Metal species	**p(TA) particles**	**Modified p(TA) particles with CHPACl**	**Modified p(TA) particles with ammonia**	
	AAS results (mg g^{-1})	**AAS results (mg g^{-1})**	**AAS results (mg g^{-1})**	**TG (Residue %)**
Co	40.0±3	38.4±2	45.8±5	9.7
Ni	35.5±0	32.3±1	36.5±3	11.9
Cu	27.1±1	26.7±1	25.1±2	12.4

Table 3. The reduction rate constants, the total turnover frequencies (TOF), and activation parameters for 4-NP, MB, and EY reduction reactions catalyzed by p(TA)-M composite IL particles (M: Co catalyst for 4-NP reduction, Cu catalyst for MB and EY reductions), at different temperatures under the same reaction conditions.

Compound	***T*** **(ºC)**	***k*** **(min^{-1})**	**Total turn over frequency (mol 4-NP mol $catalyst^{-1}$ min^{-1})**	***Ea*** **(kJ mol^{-1})**	**$\Delta H^{\#}$ (kJ mol^{-1})**	**$\Delta S^{\#}$ (J mol^{-1} K^{-1})**
4-NP	30	0.43	1.12	26.19	23.12	-182.35
	40	0.52	1.41			
	50	0.70	1.88			
	60	0.87	2.42			
	70	1.27	3.38			
MB	30	0.68	3.28	38.89	35.43	-127.54
	40	1.50	8.20			
	50	1.92	10.94			
	60	3.69	16.41			
	70	4.12	23.44			
EY	30	0.30	2.93	22.88	19.76	-188.31
	40	0.42	4.10			
	50	0.45	5.86			
	60	0.78	10.25			
	70	0.84	16.41			

Table 4. The pH and conductivity values of MB and EY solution in different media.

Compound	MB		EY	
	pH	Conductivity (μs cm^{-1})	pH	Conductivity (μs cm^{-1})
DI water	6.15±0.04	0.61±0.1	5.50±0.06	0.44±0.06
Tap water	8.08±0.05	6.27±1.2	7.60±0.03	5.87±0.8
Saricay water	8.12±0.04	285.8±4	8.36±0.04	202.6±12
Seawater	8.40±0.09	439.2±7	7.95±0.02	483±8

Table 5. The reduction rate constants, and the total turn over frequencies (TOF) of methylene blue (MB) and eosin Y (EY) catalyzed by p(TA)-Cu ILs composite in different aqueous media.

Compound	***k*** **(min^{-1})**	**Total turn over frequency (mol compound mol catalyst^{-1} min^{-1})**
MB in DI water	0.95	2.74
MB in tap water	0.86	2.05
MB in saricay water	1.40	3.28
MB in seawater	1.83	4.10
Eosin Y in DI water	0.22	1.85
Eosin Y in tap water	0.34	2.34
Eosin Y Saricay water	0.57	3.19
Eosin Y in seawater	0.66	3.74