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A novel nanocolloid system based on the poly(methyl methacrylate) nanoparticles as anticorrosive agent for boiler; a pilot-scale study

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Abstract
The boiler anti-corrosive of the present work is based on a novel phosphate-free nanocolloid containing polymethyl methacrylate (PMMA) nanoparticles, an amine compound represented by formula (NH_2—$(CH_2)_m$—O—$(CH_2)_n$—OH), (wherein each of m and n is an integer of 1 to 3), and an oxygen scavenger. The anti-corrosive was prepared by a simple mixing at ambient conditions. First, three types of microemulsion systems with different concentrations of surfactant were prepared and used to obtain three colloids of PMMA nanoparticles with a variety of particle sizes and then added to an amine/ oxygen scavenger mixture. The anti-corrosive activities of the resulting nanocolloids were used in a boiler operated with a superheater and a steam turbine, which is treated with water, is fed. The obtained results show that the used nanocolloid can more effectively maintain the pH of boiler water and prevent corrosion not only in the boiler tank but also in the entire boiler system including a feed-condensate system, without adding a large amount of phosphate salt.

Keyword: Nanocolloid, Anti-corrosion, poly(methyl methacrylate) nanoparticles, Boiler

1. Introduction

Boilers have a complex structure that is used to heat water and generate vapor. An anti-corrosive is necessary to prevent the corrosion of metal members of the boilers [1,2]. Particularly, for power generation, garbage incineration, etc., operated with a superheater or a steam turbine, ion-exchange water, reverse osmosis (RO), or desalinated water is generally used as a supplementary feed in boilers. Such boilers are generally operated at a concentration factor of about 30 to about 100, which is one of the water quality control factors. In such boilers, a phosphate salt, instead of a caustic alkali substance, is added to adjust the pH of boiler water for corrosion prevention, and a neutralizable amine or ammonia is added to elevate the pH of the boiler feed-condensate system, to thereby prevent elution of iron, whereby the amount of iron transferred into a boiler tank is reduced [2,3]. In recent years, however, the amounts of organic substances unintentionally transferred to a boiler tank have increased due to the use of various water sources and impaired water quality. In addition, the blow rate has been reduced to save energy and water, and an organic oxygen scavenger is used instead of hydrazine [3]. Under such circumstances, the pH of boiler water often lowers problematically. To solve the problem, the phosphate salt level of the boiler water is increased, or a phosphate salt-type boiler compound (a sodium phosphate-sodium hydroxide mixture) having Na/PO_4 mole ratio of 3 or higher is used. In the above case, a phosphate salt hide-out phenomenon or alkali corrosion may problematically occur [4].

The term “phosphate salt hide-out phenomenon” refers to the deposition of the phosphate salt dissolved in boiler water caused by a rapid change in concentration or pressure [3-6]. However, the anti-corrosive containing these compound have a drawback However, these compounds cannot fully elevate the pH of boiler water and also it must be added in a large amount to feed water. Thus, there is demand for an anti-corrosive that exhibits anti-corrosive performance even through the addition thereof in a small amount [6-10].

Nanotechnology can elevate the activity of anti-corrosive materials. For this purpose, Akbarian et al., tested the effects of nanoparticulate silver on the corrosion protection performance of polyurethane coatings on mild steel in sodium chloride solution [9]. The current work has been conceived for solving the aforementioned problems based on nanotechnology, and an object of the research is to provide a novel nanocolloid formulation as anti-corrosive that can more effectively maintain the pH of boiler water and which can prevent corrosion of a boiler tank and the entire boiler system including a feed-condensate system, without adding a large amount of phosphate salt. We believe that the amine compound, used in this research should have a low volatility which has high thermal stability and a high dissociation degree.

Consequently, the amine remains in boiler water rather than moving to the vapor phase, whereby the pH of boiler water can be effectively maintained and finally, the amine compound itself can serve as an anti-corrosive. To create poly(methyl methacrylate), a simple microemulsion route composed of licetin as a surfactant and capping agent that can also be acted as bio anticorrosion agent with a synergistic effect, was used.

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In continuation of our research works on microemulsion systems as a soft templates and nanoreactors for nanomaterials synthesis [11-19] the main object of the current examination is to focus on the role of microemulsion system to prepare a controllable size and morphology of PMMA nanocolloid as additive for fabrication of a novel corrosion inhibitor [20-24]. The obtained PMMA nanocolloid was characterized by DLS analysis. As a systematic investigation, the particle size of PMMA nanoparticles was also studied to test anti-corrosion behavior.

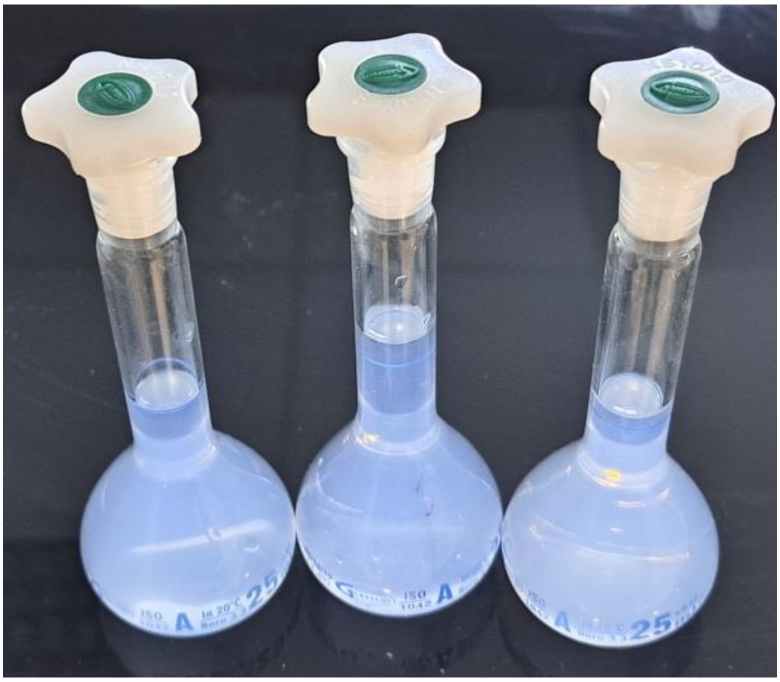
2. Experimental

2.1. Materials

Commercial lecithin ($C_{46}H_{89}NO_8P$) as surfactant to produce oil-in-Water microemulsion, methyl methacrylate monomer ($CH_2C(CH_3)COOCH_3$) (AR grade), were purchased from Merck Company and 2-(2-aminoethoxy)ethanol as amine source was purchased from Sigma-Aldrich. Potassium persulfate as an hydrophilic initiator for polymerization of MMA was purchased from Haihang Industry Co. LTD, and sodium metabisulfite was received from Qingdao Tianya Chemical Co., Ltd. Deionized water (0.055 µS/cm) which was produced in our lab with PKA (Smart two pure) instrument.

2.2. PMMA nanocolloid preparation

To prepare PMMA nanocolloid, two oil-in-water microemulsion system consisting of aspartic acid and glutamic acid as surfactant, MMA as apolar phase, and water should be obtained. In this procedure, at the first time two clear aqueous solution of surfactants with concentrations of the 0.02 M were prepared. After that, same as our previous works, the adjusted amount of the MMA that was fixed at 2%Wt was added to surfactant solutions and were vigorously stirred to form MMA-in-Water reverse microemulsions. Potassium persulfate as an oxidizing agent were added to the two above amino acid stabilized MMA colloidal systems and all vials were put at 60°C for 4 h to start the polymerization process [27-30]. Finally, the cloudy and stable PMMA colloid was obtained that this color change confirmed the synthesis of the PMMA nanoparticles in amino acid based-micelles was successful. Then the prepared PMMA nanocolloids were abeled as CG and CA based on the name of the usage amino acids (CG for colloid prepared with glutamic acid and CA for colloid prepared with aspartic acid) and then characterized with DLS analysis. Fig. 1 shows the prepared PMMA nanocolloids at different surfactant types.



(a) (b) (c)

Fig. 1. The PMMA nanocolloids prepared based on the microemulsion system at different surfactant types (a) glutamic acid (CG) (b) aspartic acid (CA).

2.3. Preparation of the anti-corrosion inhibitor

To prepare anti-corrosion inhibitors, two mixture of 2-(2-aminoethoxy)ethanol (3 g) and sodium metabisulfite (6.5 g) as oxygen scavengers was prepared, separately. Then 0.5 ml of both PMMA nanocolloids composed of CG and CA samples were added to both mixtures. Finally, a fine powder was obtained and aged at room temperature. As a control sample, a sample was prepared without PMMA nanocolloid to approve the role of PMMA nanoparticles capped with glutamic and aspartic acid stabilizing agent.

2.4. Preparation of anti-corrosion-PMMA colloid

For this purpose, 100 g of the both above-mentioned powders were dissolved in 1 L pure water (ion-exchange water) feed and used for the corrosion tests in boiler.

2.5. Characterization of PMMA nanocolloid

To confirm and determine of average particle size and polydispersity index (PDI) of both samples (CG and CA) DLS analysis as a common technique with Bettersize (Optical nanoparticle size analyzer Nanoptic 90) were employed. Before DLS analysis, all samples (CG and CA) were sonicated for 6 min at room temperature.

2.6. Corrosion study

Based on the our previous report, a test boiler which was operated under the following conditions: a pressure of 4 MPa, a blow rate of 1%, a condensate recovery of 20%, pure water (ion-exchange water) feed, and use of a heater-degasser [outlet degassing capacity (dissolved oxygen level: DO) of 0.03 mg/L] was used to study the corrosion tests. In the corrosion test, to the feed water, the anti-corrosion-PMMA colloid with different PMMA nanocolloids (CG nad CA) in the formulation of inhibitor were added in an amount of 10 mg/L, separately. As a result, the pH of boiler water was 10.20-10.57.

During the test period of one week, the boiler was operated for 5 days and stopped for 2 days. The procedure was repeated. That is, the test was performed for 14 days. By the above test, the iron level of the feed water (average) (mg/L), the amount of iron deposited on the thermal conduction surface (mg Fe/cm^2), and the corrosion rate (mdd) of a steel test piece placed in the test boiler were evaluated for both anti-corrosion inhibitors.

As a comparative study, the corrosion study was tested in the same condition but with a solution composed of 2-(2-aminoethoxy)ethanol, sodium metabisulfite, and water without PMMA nanoparticles. The unit (mdd) of the corrosion rate of a test piece is based on the daily amount of corrosion (mg) for an area of 100 cm^2.

Test piece corrosion rate (mdd) was calculated based on the thickness measurement data with Thickness Meter PCE-CT 80-FN0D5 with accuracy after foil calibration: ±(1% of reading + 1 µm); for many materials such as iron, steel, aluminum, copper, brass, stainless steel; Diameter: 17mm / 0.67). Iron Determination by colorimetric method Using O-Phenanthroline was performed [30].

3. Result and discussion

3.1. DLS analysis

Fig. 2-(a-c) shows the DLS analysis of both PMMA nanocolloid prepared in microemulsion with different stabilizing agents composed of glutamic acid and aspartic acid. DLS particle size analyzers are used to measure the size and hydrodynamic radius (Rh) of very small particles (0.6 nm to 6 um) in solution. The particle size range of DLS depends on the properties of the analyzed species, such as refractive index or density, as well as the surrounding formulation, mainly the viscosity. As can be seen from Fig. 2, it is clear that the PMMA particle size controlling is mainly dependent on stabilizing agent type, and when the capping agent is glutamic acid the PMMA particle size is 92 nm that it is bigger than aspartic acid (78 nm) due to smaller molecular size rather to glutamic acid that were introduced in Schem. 1.

Based on intensity fluctuations of laser light scattered by the molecules/particles, moving in Brownian motion, the diffusion coefficient is determined and converted to particle size via the Stokes-Einstein equation. DLS can determine the hydrodynamic size of protein monomers, small aggregates in the nanometer range and partially also particles in the high nanometer/low micrometer range. The technique can also be employed for the analysis of colloidal systems, such as liposomes, nanoparticles, polymers and virus-like particles.

The DLS data evidenced that the optimum surfactant concentration in microemulsion due to the formation of PMMA with smaller particle size (about 67 nm, Fig. 2-b), is 0.02 M. After collisions between droplets of MMA monomer and oxidizing agent molecules the polymerization started and PMMA nanoparticles are produced. The local distribution of the PMMA nanoparticles in water containing lecithin surfactant may be related to the exchange rate of PMMA nuclei between microemulsion droplets. The dynamic exchange process of the reactants in different microemulsion droplets plays an important role in controlling the particle size and distribution [20].

The most particle size was observed for the microemulsion that was prepared by 0.03 M surfactant (174 nm, Fig. 2-(c). The reason for this phenomenon can be described as follows; by increasing the concentration of surfactant, the number of formed MMA micelle droplets is increased. So, more collisions between droplets of MMA monomer were done and leds to the formation of bigger PMMA particle size. The mechanism of the nanoparticle formation and growth in the microemulsion systems is shown schematically in Fig. 3.

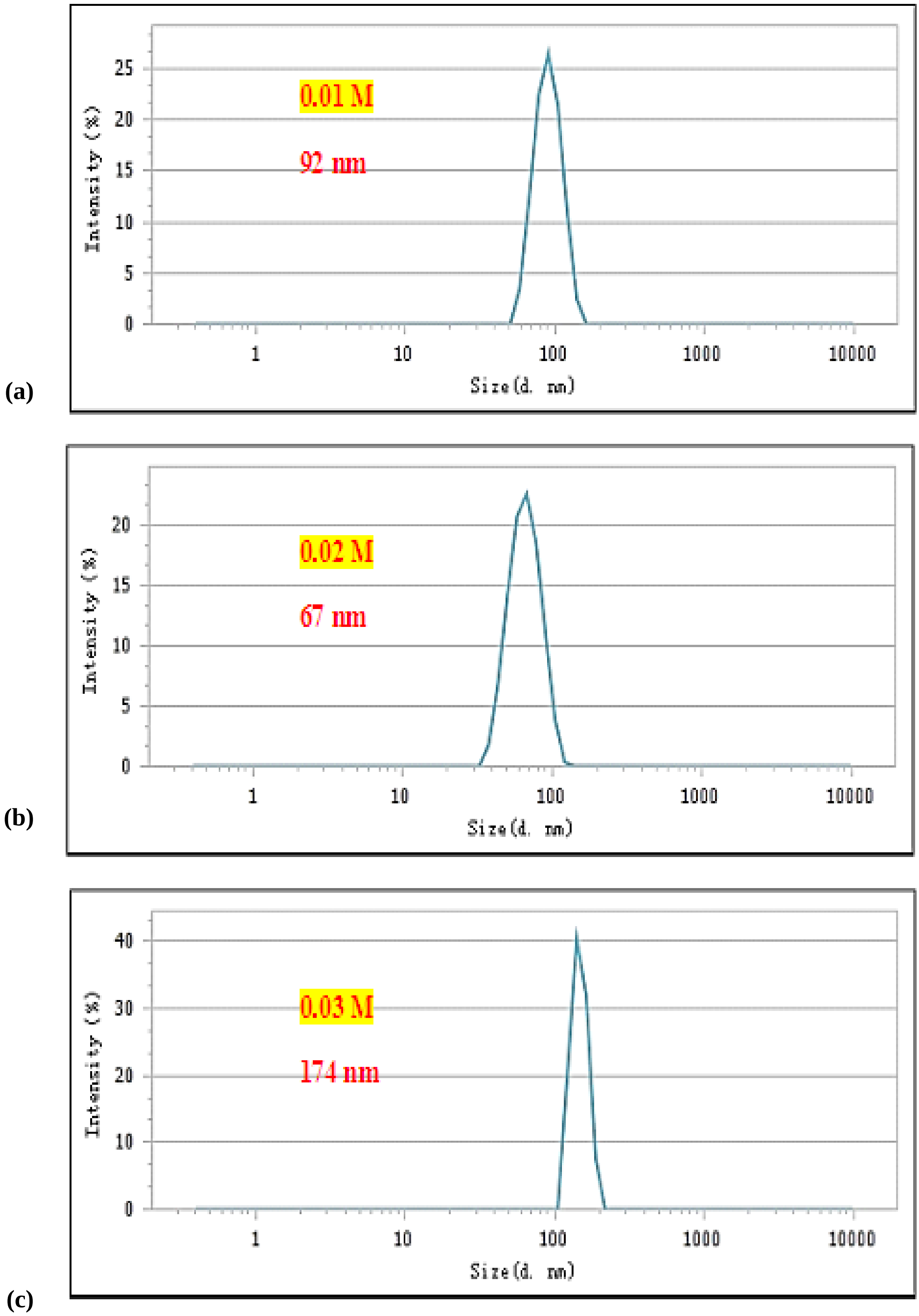


Fig. 2. DLS analysis of all samples with different surfactant concentration containing (a) 0.01 M, (b) 0.02 M, and (c) 0.03 M.

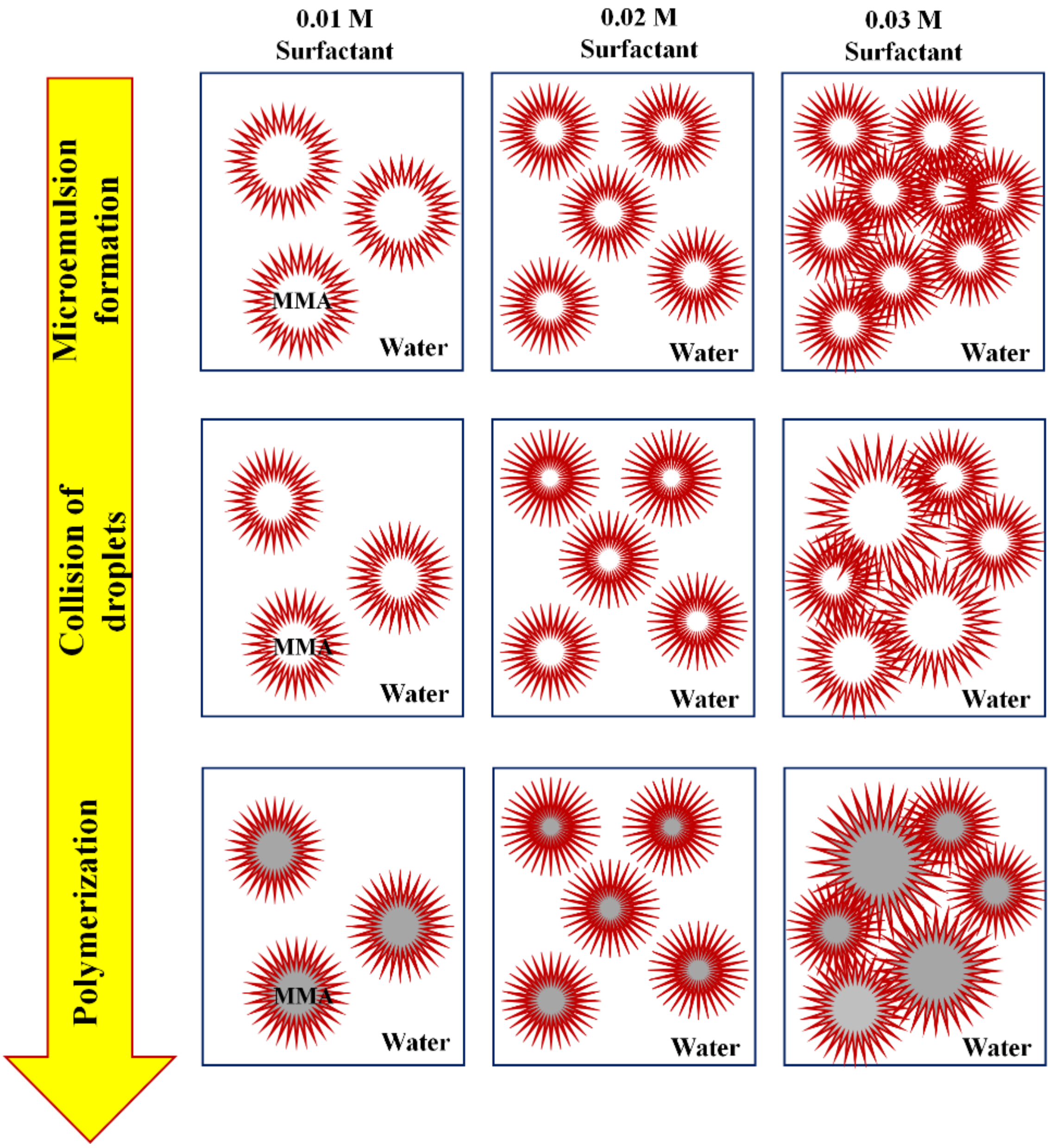


Fig. 3. The mechanism of the PMMA nanoparticles formation and grown in the MMA-in-Water microemulsion systems.

3.2. Corrosion study

Fig. 4-(a-c) the corrosion investigation based on the Fe level of feed water (mg/L), amount of Fe deposited on the thermal conduction surface (mg Fe/cm^2), and test piece corrosion rate was examined. As can be seen from Fig. 4, it was confirmed that the prepared corrosion inhibitor prepared by PMMA nanocolloid with particle size of 67 nm (P67) has the best anti-corrosion performances for boiler in all test (Fe level of feed water, amount of Fe deposited and corrosion rate). The reason for this event relates to the increase of the PMMA surface area that is capped with lecithin molecules. The carbonyl group of PMMA coordination with amine provided stable complexes against diffused oxygen. The interaction of lecithin molecules and amine molecules led to create a nanometric layer on the surface of metal. The nanometric layer coated on the surface of the boiler is highly strong under dissolved oxygen and more effectively protects the surface of the boiler. Other samples P92 and P174 that were prepared with bigger PMMA sizes have weak anti-corrosive activity in the same condition for three tests.

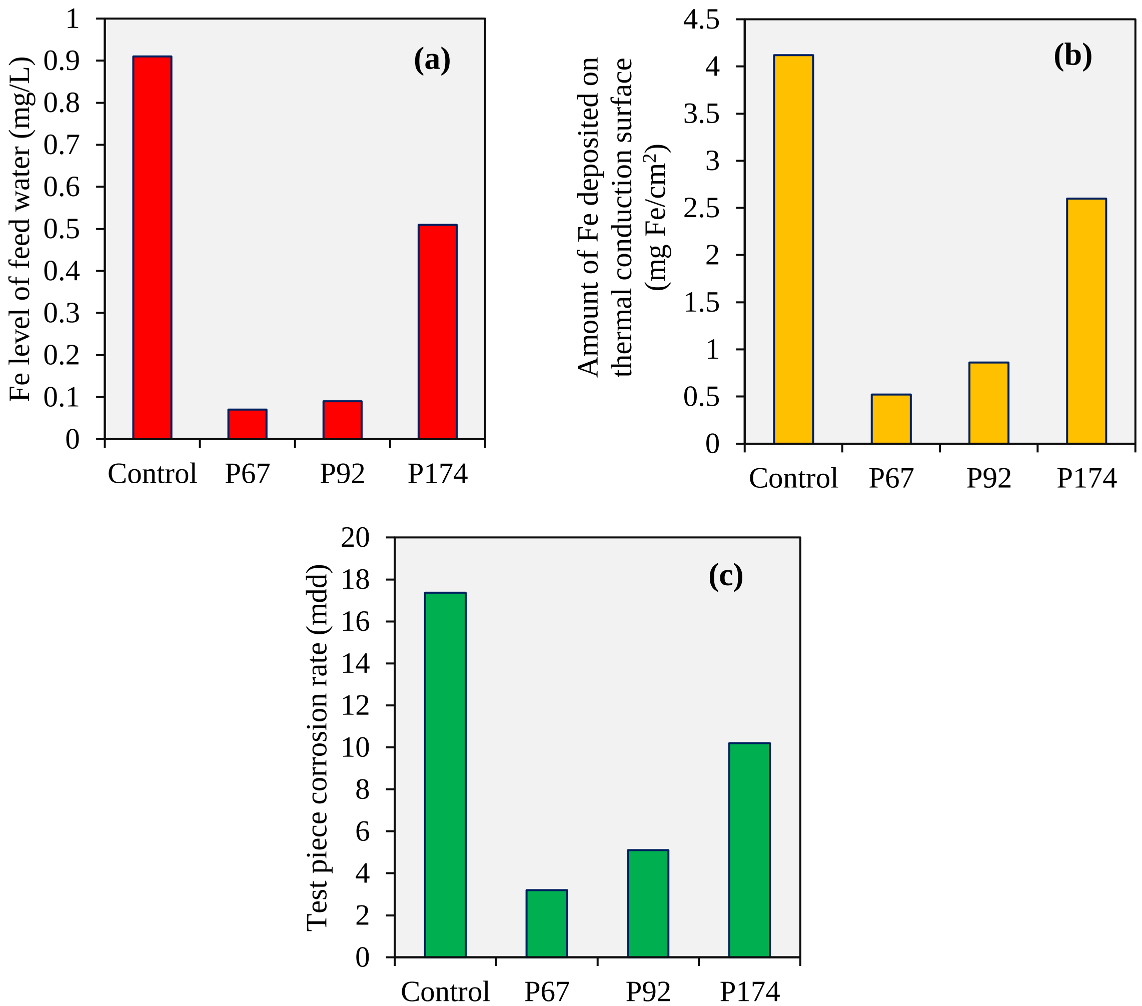


Fig. 4. (a) Fe level of feed water (mg/L), (b) Amount of Fe deposited on thermal conduction surface (mg Fe/cm^2) and test piece corrosion rate (mdd)

4. Conclusion

In order to attain in production of the anti-corrosion material extensive studies are conducted. In this work, it is found that these materials can be attained by a unique combination of nanotechnology by preparation of polymeric nanocolloid and an amine compound having a specific structure including an amino group and a hydroxyl group in the molecule thereof, in particular, a chemical agent containing an oxygen scavenger and the agent containing the amine compound. In this research, three types of polymeric nanocolloids based on the PMMA nanoparticles with a variety of particle sizes were prepared by a microemulsion system and were tested to understand the anti-corrosive activity. The results show that the anti-corrosion formulation produced with PMMA nanocolloid with smaller particle size has the best performance.

Conflicts of Interest

The author declares no conflict of interest.

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