Synthesis and characterization of ammonium polymer for anion removal in aqueous solutions

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Abstract: In a one-step thermal process using 2-[(methacryloyloxy)ethyl]trimethylammonium chloride (META), an ammonium polymer was successfully obtained for the removal of anions (nitrates, nitrites, and phosphates) from aqueous solutions. Ethylene dimethacrylate (EDMA) was used as a cross-linking agent. The effect of cross-linking agent, porogen, and polymerization time on the structure and physical properties of the obtained polymer was examined (FTIR, SEM, BET, elemental analysis). The optimal conditions for META synthesis were a monomer to porogen ratio of 20:80, 75% functional monomer content and a 12-hour polymerization time.

Keywords: ammonium polymer, nitrate, nitrite, one-pot approach, phosphate.

Synteza i charakterystyka polimeru aminowego do usuwania anionów z roztworów wodnych

Streszczenie: W jednoetapowym procesie termicznym przy użyciu chlorku 2-[(metakryloiloksy)etylo] trimetyloamoniowego (META) otrzymano polimer amoniowy do usuwania anionów (azotanów, azotynów i fosforanów) z roztworów wodnych. Jako środek sieciujący zastosowano dimetakrylan etylenu (EDMA). Zbadano wpływ środka sieciującego, porogenu i czasu polimeryzacji na strukturę i właściwości fizyczne otrzymanego polimeru (FTIR, SEM, BET, analiza elementarna). Jako optymalne warunki syntezy META przyjęto stosunek monomeru do porogenu 20:80, 75% procentową zawartość monomeru funkcyjnego i 12-godzinny czas polimeryzacji.

Słowa kluczowe: polimer aminowy, azotany, azotyny, synteza jednonaczyniowa, fosforany.

A polymer is a substantial molecule comprising several monomers joined by cross-binders [1]. Polymers are typically employed as the primary component of plastics, and scientists have conducted many studies on using polymers as adsorbents for removing ions in liquid waste. This kind of waste contains a complex mixture of inorganic and organic ions with a high potential for contamination. Some major pollutants in water bodies include nitrates, nitrites, and phosphates emitted from fertilizers, compost, and animal and human waste. When the concentration of these compounds in shallow waters is exceeds the norms, it will reduce agricultural potential of soil and cause algae overgrowth on water. Consequently, the algae blooms reduces concentration of dissolved oxygen in the water causing sudden suffocation of fish and other aquatic plants and animals [2, 3]. This dangerous phenomenon also leads to water clarity reduction, decreasing overall water quality, affecting ecological balance [4].

Adsorption is one of the best techniques for reducing or even eliminating toxin ions from wastewater. Ion exchange procedure have been tested in several studies as a way to treat water and waste polluted with nitrate and phosphate ions. As a result, it has been discovered that concentration of these pollutants may be reduced. Due to its efficiency, the ion exchange method becomes a reference for separating pollutant compounds found in wastewater with advanced material-based adsorption media as a polymer. Several polymers have been developed and used as adsorbents in adsorbing some heavy metals, both in the form of ions and organic compounds. Adsorption of Cr(VI) ions has been performed using magnetic polymers containing amino groups [5, 6]. Methacrylate-based organic polymers with the opening epoxy ring method were also successfully applied for the adsorption of Cu(II) [7] and Hg(II) ions [8, 9]. Polymers have been used successfully to adsorb organic compounds like phenol [10], bisphenol A (BPA) [11], and pentachlorophenol in addition to ions [12, 13].

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Polymer production is often divided into two stages: polymerization and post-modification. The synthesis of organic polymers commonly involves polymerization reactions [14], which can be classified into two main categories: chain-growth polymerizations and step-growth polymerizations. This classification is based on how the chemical process of chain creation occurs. Otherwise, the post-modification has some disadvantages: time-consuming manufacturing and a limited variety of polymer-forming materials [1].

The latest approach in polymerization techniques is a simple one-step method known as the one-pot approach. The one-pot approach was introduced as a new strategy for a more effective and sophisticated way of preparing monolithic columns in the polymerization process. Compared to conventional polymerization methods, the polymerization process with one-step method has the advantages of being environmentally friendly, simple, easy to develop, and not taking a long time in stages. In addition, this method is low-cost because it does not require any advanced modification stages. In contrast, other polymerization methods still require further modification at the final stage [15, 16].

Several studies have conducted polymer synthesis by one-pot approach technique using a variety of functional monomers. One of the functional monomers is 2-[(methacryloyloxy)ethyl]trimethylammonium chloride (META). META and ethylene dimethacrylate as crosslinker have been prepared as monolith organic polymer using a simple single thermal using one-pot approach method [1]. However, these experiments have not applied for adsorption materials.

The one-pot approach has become widely used in producing stationary-phase materials on liquid chromatography columns. Nonetheless, only a few companies use it to develop materials for adsorption that will be used as adsorbents for the simultaneous removal of contaminating ions. To the best of our knowledge, the development of META polymer as adsorbent by one-pot approach technique for anion removal in aqueous solutions has not been conducted before.

The aim of this research was to synthesize a polymer containing quaternary amine groups introduced from META by a fast, simple and uncomplicated method known as the one-pot approach. The surface structure of the obtained polymer was examined using FTIR, SEM, BET and elemental analysis.

EXPERIMENTAL PART

Materials

2-[methacryloyloxy)ethyl]trimethylammonium chloride solution (META) was purchased from Sigma Aldrich. Ethylene dimethacrylate (EDMA), and 2,2′-azobisisobutyronitrile (AIBN) were supplied by TCI (China). Isopropyl alcohol (IPA), poly(ethylene glycol) with

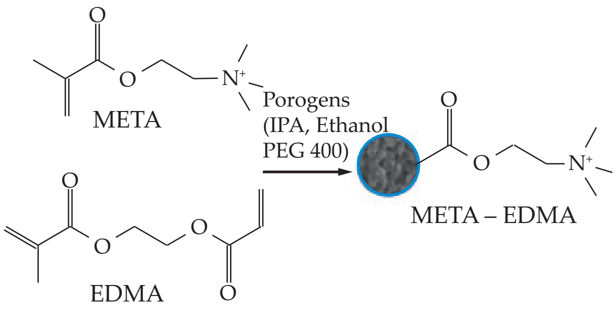

Fig. 1. Scheme of META polymer expected reaction

M_n = 400 (PEG 400), ethanol, $NaNO_3$, $NaNO_2$ and Na_3PO_4 were purchased from Wako 1st Grade, Japan.

Methods

Synthesis of META polymer

Initially, the polymerization stage was carried out by preparing a mixture solution according to previous research with major modification by Rahayu [1], with the scheme of expected reaction shown in Figure 1. The mixture solution was 1.25 mL of META, 0.375 mL of EDMA, 1.75 mL of isopropyl alcohol (IPA), 0.35 mL of ethanol, 1.4 mL of PEG, and 2 mg AIBN, then was homogenized before filling into the cylinder tube. Subsequently, the polymerization was allowed at 70°C for 24 hours in the water bath. The obtained polymer was rinsed with methanol to remove the residual reaction. The process was optimized by observing several conditions that affect the polymerization process: the ratio monomer to porogen (10:90, 20:80, 30:70 and 40:60), the percentage of functional monomer (25%, 50%, and 75% of META) and polymerization time (4, 6, 12, and 18 hours).

Characterization of META polymers as adsorbents in aqueous solution

Identification of the functional group in META polymer was carried out using Fourier transform infrared (FTIR) Spectrum 400 Series Perkin Elmer (Waltham, Massachusetts, USA). Scanning electron microscope (SEM) instruments (Hitachi SU3500, Tokyo, Japan) were used to investigate the morphology of ammonium polymer. Elemental analysis was carried out by using MT-6 CHN Corder (Yanaco, Kyoto, Japan). A surface area analyzer (SAA) (Quantachrome Novatouch Lx4) was used to analyze polymer surface area and its porous dimension distribution.

Application for removal anion in the aqueous solution

The optimum META polymer was applied to remove the anions in an aqueous solution simultaneously. It was started with 25 mL of an aqueous solution containing 15 ppm of nitrates, nitrites, and phosphates,

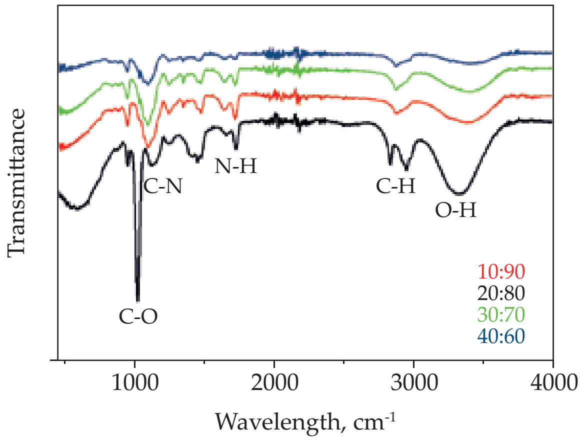

Fig. 2. FTIR spectra of META polymers with different monomer and porogen ratio

and then contacted with 0.5 g of META for 20 minutes and at room temperature. The measurement of nitrate, nitrite and phosphate concentration was conducted using Spectrophotometry UV-Vis (Thermo Scientific Genesys) at a wavelength of 450 nm. The efficiency of removal and capacity factor (q_e) were calculated using equation 1 and 2, respectively.

$$q_e = \frac{(C_0 - C_e) \cdot V}{C_0} \tag{1}$$

$$\text{Efficiency of removal} = \frac{C_0 - C_e}{C_0} \cdot 100\% \tag{2}$$

where: C_0 represents the initial concentration of the adsorbate solution (mg/L), and C_e for its equilibrium concentration (mg/L), respectively; W is the weight of the adsorbent (g), and V is the volume of solution (L).

RESULTS AND DISCUSSION

Effect of monomer and porogen ratio

The monomer to porogen ratio was investigated, maintaining the percentage of cross-linker. The monomer to porogen ratio was 10:90, 20:80, 30:70 and 40:60. Three organic compounds acted as porogens: isopropyl alcohol, polyethylene glycol, and ethanol, which formed macropores on the polymer surface. FTIR spectra of META polymer differing in monomer and porogen ratio are presented in Figure 2. The strong band appearing in the region of 1080–1113 cm^{-1} corresponds to the stretch-

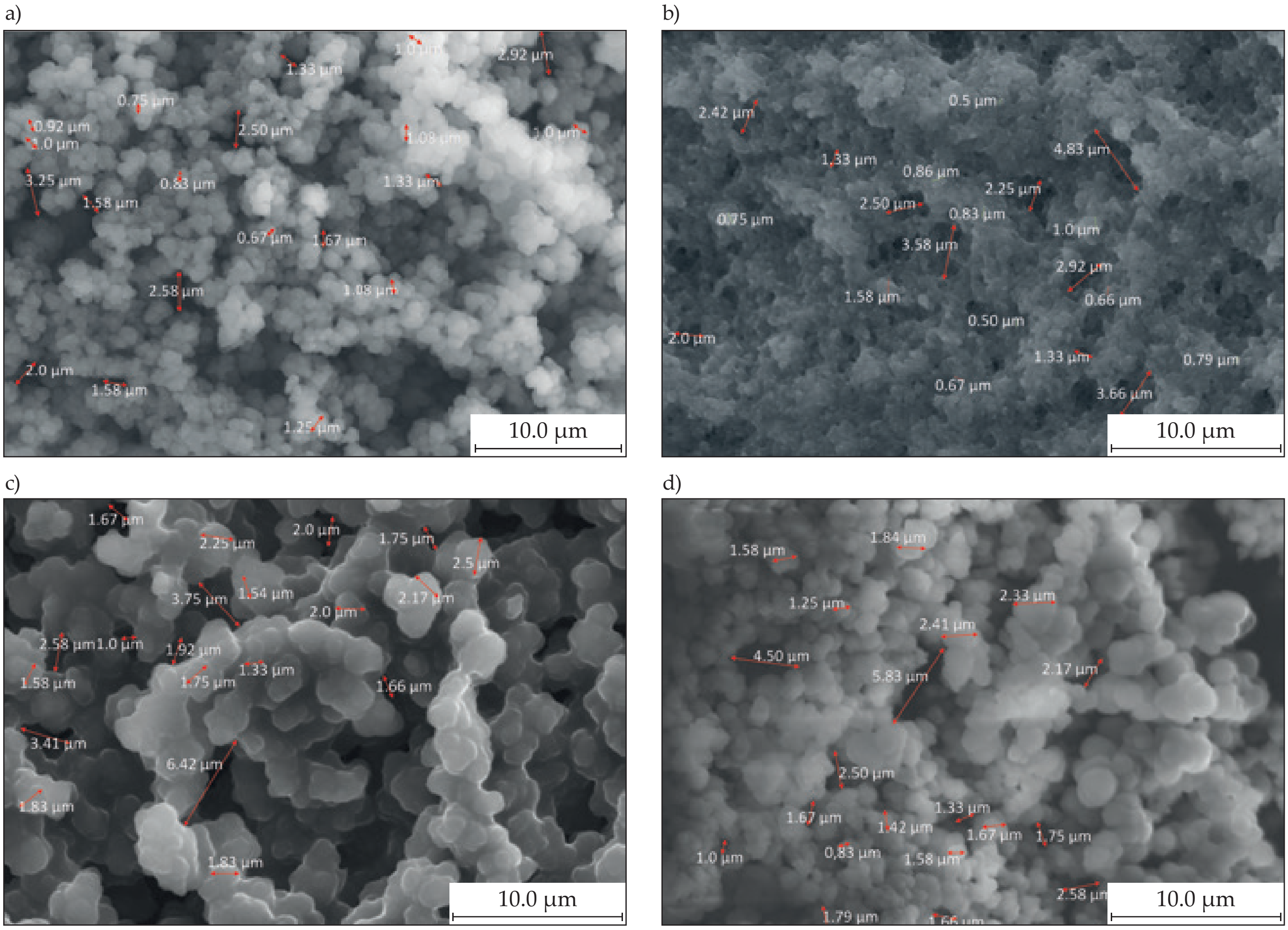

Fig. 3. SEM images of META polymers with different monomer and porogen ratio: a) 20:80, b) 30:70, c) 40:60, d) 10:90

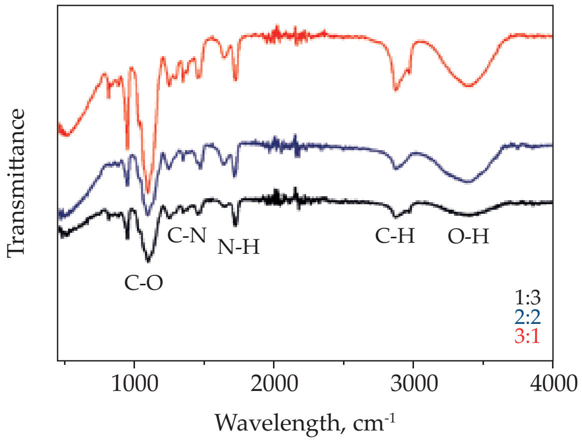

Fig. 4. FTIR spectra of META polymers with different monomer ratio

ing vibrations of the C-O group. Furthermore, the bands observed in the region of 1220–1247 cm^{-1}, 1643–1650 cm^{-1}, 2858–2945 cm^{-1} and 3328–3402 cm^{-1} correspond to the vibrations of the C-N, N-H, C-H and OH groups, respectively. There are differences in peak intensity depending on monomer to porogen ratio. The strongest peak was observed at about at 1100 cm^{-1} for 20:80 monomer to porogen ratio, which means that 20% was a mixture of monomer and cross-linker and 80% was porogen. FTIR results suggest that a monomer to porogen ratio of 20:80 is optimal for the polymerization process.

The distribution of unions and macropores in the META polymer is shown in Figure 3. The macropores were significantly formed and evenly distributed. The range size for the union for ratios 20:80, 30:70, 40:60, and 10:90 is 0.92–1.08 µm, 0.5–1.58 µm, 1.33–2.50 µm, and 0.83–2.41 µm, respectively. Meanwhile, the range size for the macropore for ratios 20:80, 30:70, 40:60, and 10:90 is 1.33–3.25 µm, 1.33–4.83 µm, 1.66–6.42 µm, and 1.00–4.50 µm, respectively. The best monomer to porogen ratio is 20:80. Polymers used in a three-dimensional approach are processed into microporous and/or nanoporous cell carriers with various structures and properties [17, 18].

Effect of META percentage

The availability of the monomer META in this polymerization will also be critical because META has an ammonium quaternary functional group. Since META is the monomer and directly introduced to ammonium

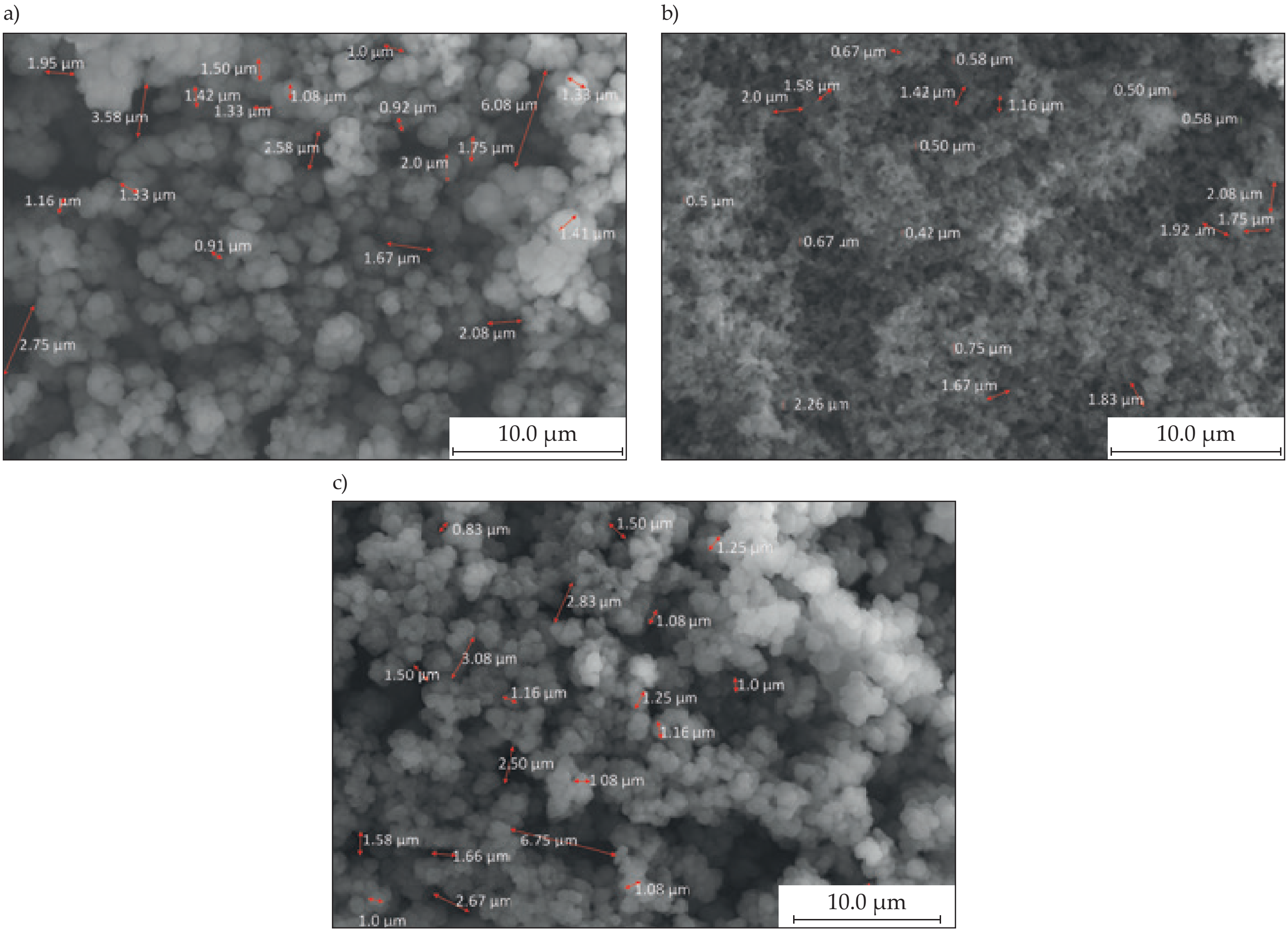
a)
b)
c)

Fig. 5. SEM images of META polymers with different META content: a) 25%, b) 50%, c) 75%

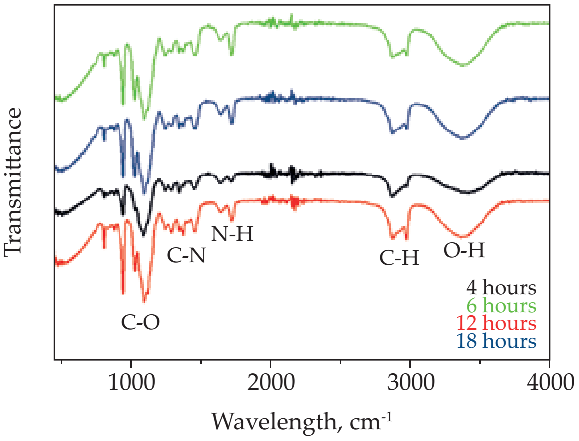

Fig. 6. FTIR spectra for different polymerization time

quaternary group, more reactive groups will be available as anion exchanger sites when the percentage of META in the mixture solution is increased. On the other hand, EDMA is a highly reactive cross-linker containing ethylene bridge. Figure 4 shows the FTIR spectra of 25%, 50%, and 75% of META in ammonium polymer.

In Figure 4, the peak in the region of 1086–1093 cm^{-1} is associated to the C-O group (stretching), the peak in the region of 1040–1247 cm^{-1} is corresponded to C-N, the peak in the region of 1630–1643 cm^{-1} is associated to the N-H group, the peak in the region of 2858–2871 cm^{-1} is connected to the C-H (stretching) and the peak in the region of 3388–3402 cm^{-1} is related to the O-H group. The spectrum of the polymer containing 75% META has the sharpest peak among the others peaks, thus meaning the optimal amount of META in the polymer solution. Figure 5 shows the distribution of unions and macropores in the META polymer with variations in the percentage of META. The macropores were significantly formed and evenly distributed. The range sizes for the union for 25%, 50%, and 75% META content were 0.91–2.00 µm, 0.5–2.00 µm, and 1.00-2.08 µm, respectively. Meanwhile, the range sizes for the macropore for 25%, 50%, and 75% META content, were 0.91–2.00 µm, 0.5–1.41 µm, and 0.83–2.41 µm, respectively.

According to the FTIR and SEM results, the polymer containing 75% META had the best structure. The obtained results are consistent with Cockram work [19].

Effect of polymerization time

The structure of META polymers depended on the polymerization time, as evidenced by the different inten-

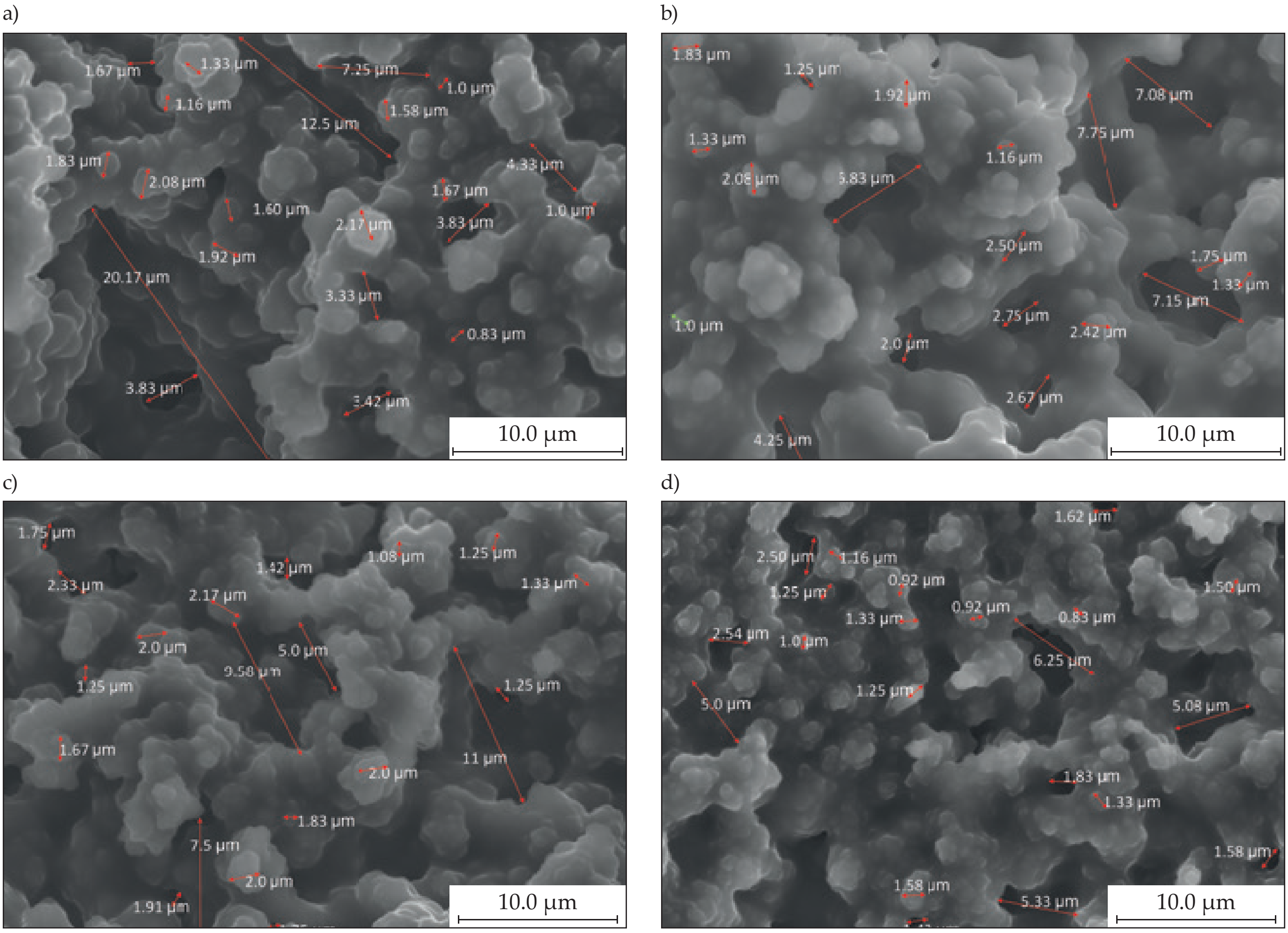

Fig. 7. SEM images of META polymers for different polymerization time: a) 4 h, b) 6 h, c) 12 h, d) 18 h

sity of characteristic peaks in the FTIR spectra (Fig. 6). The process was carried out for 4, 6, 12 and 18 hours. The polymer obtained in a process lasting 12 hours was characterized by the strongest peaks intensity. This indicates that the optimal polymerization time is 12 hours.

Figure 7 shows the morphology of META polymer with various polymerization times. The distribution macropores in the META polymer were significantly formed and evenly distributed. The range size for the union for polymerization time (4, 6, 12 and 18 h) is 0.83–2.08 m, 1.00-2.24 m, 1.33-2.17 m, and 0.83-1.50 m, respectively. Meanwhile, the range size for the macropore for the time of polymerization (4, 6, 12 and 18 h) is 1.00–12.5 m, 2.00–7.75 m, 2.33–11.00 m, and 1.42–5.33 m, respectively. The polymer obtained in a process lasting 12 h was characterized by the most uniform porous structure. SEM images confirmed the FTIR results, indicating that the optimal polymerization time was 12 hours. These findings are consistent with research conducted by Lei [20], who believes that a polymerization process time of 12 hours results in better adsorption.

Repeatability of META polymer polymerization

The repeatability of the specific surface area, volume and pore size of the META polymer obtained under optimal conditions is shown in Table 1. The relative standard deviation (RSD) of the specific surface area, total volume and pore size was found to be 0.20%, 0.13% and 0.86%, respectively, which confirms the good repeatability of the results obtained.

Table 1. Repeatability of META polymer polymerization

Sample	Surface area m^2/g	Total pore volume mL/g	Pore size nm
R-1	5.6992	0.0044	1.55381
R-2	4.8382	0.0040	1.65148
R-3	3.7268	0.0034	1.82255

Application to the aqueous solution

In a prior study, META polymer was successfully used as a stationary phase for separating organic molecules utilizing a liquid chromatography system [1]. In this research, the META polymer will be applied as an adsorbent to remove anions in aqueous solution. According to the BET analysis (Table 1), the optimum surface area, volume pores, and pores size are 5.6992 m^2/g, 0.0044 mL/g, and 1.82255 nm, respectively. The percentage weights of carbon, hydrogen, and nitrogen in META polymer were determined by elemental analysis. The percentages weight of carbon, hydrogen, and nitrogen were 8.57, 46.95, and 3.77, respectively. The polymer contains nitrogen, introducing a quaternary ammonium compound that acted as a strong anion exchanger. Furthermore, this strong anion exchanger potentially reacted with a negative site from ion nitrate, nitrite, and phosphate in an aqueous solution. The performance of META polymer for eliminating ion nitrate, nitrite and phosphate in aqueous solution are demonstrated in Figure 8.

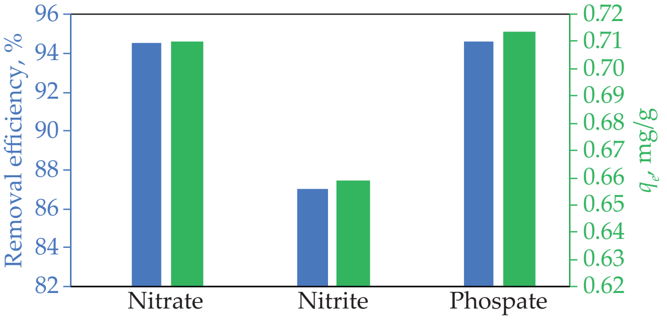

Fig. 8. Efficiency and adsorption capacity of nitrate, nitrite, and phosphate in an aqueous solution by META polymer

The efficiency of META polymer in removing nitrate, nitrite and phosphate ions was 94.58%, 87.44% and 95.11%, respectively, and the anions removal efficiency coefficient (q_e) was 0.71, 0.66 and 0.71, respectively. The results prove that ammonium polymers can be used for the adsorption of ions in aqueous solutions. The RSD for the removal of nitrate, nitrite and phosphate ions was found to be 0.05%, 0.84% and 0.4%, respectively.

CONCLUSIONS

META polymer with a strong anion exchanger was successfully synthesized using a one-pot method. The optimal polymerization conditions for the META polymer were obtained with a monomer to porogen ratio of 20:80, 75% functional monomer content, and 12 hours of polymerization. FTIR, SEM, BET and elemental analysis showed that the META polymer is a potentially alternative adsorbent for the adsorption of nitrate, nitrite, and phosphate ions in aqueous solutions. In future studies, it is suggested to use this adsorbent for wastewater containing nitrate, nitrite, and phosphate ions.

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