

Adhesion Enhancement of Poly (acrylamide -co- Acrylic Acid)/ Polyethylene Glycol anti-Biofouling Coating using Fly Ash based Geopolymer

Siti Musliha Mat Ghani^a, Lieding Abdul Mutalib^a, Nurul Ekmi Rabat^{b,*}, Ros Azlinawati Ramli^c, Muhammad Rashid Shamsuddin^a, Man Kee Lam^a

^aChemical Engineering Department, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak

^bCenter of Contaminant Management and Utilization, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak

^cFaculty of Industrial Science and Technology, Universiti Malaysia Pahang, Gambang, 26300, Kuantan, Pahang
nurulekmi.rabat@utp.edu.my

Hydrogel has been used as an alternative to replace biocide-based paint in preventing biofouling. However, hydrogel has low adhesion on metallic substrate, hindering its application for coating. Therefore, the aim of this project is to enhance the adhesion strength and anti-biofouling properties of the poly(acrylamide-co-acrylic acid)/polyethylene-glycol hydrogel, poly(AAm-co-AAc/EG) coating via the incorporation of fly ash-based geopolymer that range from 0.5 wt% to 2.5 wt%. The hydrogel coating was synthesised via free radical polymerisation with the aid of N,N-methylenebisacrylamide (MBA) as the crosslinker, and ammonium persulfate (APS) as the initiator. The Fourier transform infrared (FTIR) spectra of the hybrid hydrogel had proved the presence of geopolymer with the availability of significant peaks at 3,294 cm⁻¹ (N-H bond), 2,946 cm⁻¹ (O-H bond), 1,545 cm⁻¹ (C-O-C bond) and 1,113 cm⁻¹ (Si-O-Si or Al-O-Si bond). The average swelling capacity of the hybrid hydrogel coating in distilled water (up to 50,000 %) was significantly higher than in artificial seawater (up to 5,000 %) due to osmotic pressure difference. The anti-biofouling performance test by using algae (*Chlorella vulgaris* sp.) suspension showed that the incorporation of 2.0 wt% geopolymer into hybrid hydrogel coating had successfully reduced the algae attachment on the substrate by 92 % as compared to the control sample. The adhesion strength of all hydrogel coatings was investigated by using the pull-off adhesion test in accordance to ASTM D4541. The incorporation of 2.0 wt% geopolymer into hydrogel matrices demonstrated an increment of 58% in adhesion strength on steel plate as compared to neat hydrogel. The results showed that geopolymer has the potential to improve the anti-biofouling and adhesion strength of hydrogel coating.

1. Introduction

Biofouling has been a major issue which negatively affects several fields, including medical area, water treatment system and marine industry. Generally, biofouling is a natural occurrence that is associated with the undesirable deposition or attachment of aquatic or semi-aquatic microorganisms on the surface of property, such as submerged pipelines and product-transporting ships (Nurioglu et al., 2015). The consequences of biofouling can be seen in the form of corrosion on the surface of material by microbial activity. Biofouling also results in additional fuel consumption that is needed to compensate the kinetic energy loss. The kinetic energy loss is due to increase in friction by the significantly rough layers naturally made by the biological creatures on the transportation surface which then leads to increase in carbon emission into the atmosphere (Taylor et al., 2011).

There are several methods to prevent or minimise the unwanted biological deposition on the material surface. One method is by applying protective anti-biofouling paints. These paints are embedded with biocides, such as biotoxin organotin and copper-based compound to inhibit the microbial activity of targeted organisms that is related to the formation of biofouling. A problem that soon became apparent was the short service life due to rapid leaching and accumulation of copper salts in the aquatic environment (Telegdi et al., 2016). Another

widely used biocide, which is tributyltin (TBT), was banned since 2008 because it caused the bioaccumulation of tin in fish and masculinisation in female stenoglossan gastropod species (Taylor et al., 2011). Therefore, the non-biocide coating has become in demand.

Hydrogel coating is known as an environmentally friendly alternative to replace biocide coating. The hydrogel is a three-dimensional polymer matrix that can take up and retain a large amount of water (Fregolente et al., 2018). Due to the high hydrophilicity possessed by the hydrogel, it creates a hydration barrier which is made of water molecules, forming a shield against biofoulants (Telegdi et al., 2016). For example, sulfonate was used to enhance the hydration effect of polyvinyl alcohol and decrease in green algae and diatom accumulation densities were observed (Yang et al., 2017). The low adhesion of hydrogel on a substrate is a challenge for hydrogel application as an anti-biofouling coating. Studies on hydrogel adhesion improvement were more on mimicking the adhesion of mussels by using amino acid 3,4-dihydroxy-L-phenylalanine (L-dopa) (Gao et al., 2018) or by using siloxane-based compound (Bodkhe et al., 2014). These two compounds showed a significant improvement in the adhesion between hydrogel and substrate, but these materials are expensive. In creating a more sustainable material and environment, fly ash-based geopolymer was studied as a possible solution in solving the adhesion issue of hydrogel coating on a metallic substrate. Fly ashes are waste materials which result from the burning of pulverised coal which accounts for 65%–85%. Geopolymer is the product of reaction between aluminosilicate material like fly ash and strong alkaline solution. As coating filler, the incorporation of geopolymer in hydrogel matrices has the potential to solve the low-adhesion issue. The availability of SiO in geopolymer creates a strong bond between the metallic substrate and coating through the Si-O-M bond; M represents the metallic substrate which is the main component of underwater structures (Ueng et al., 2012). Therefore, this study focuses on the synthesis of the hybrid hydrogel anti-biofouling coating through the incorporation of fly ash-based geopolymer into the coating to increase the adhesive property between hydrogel coating and substrate. The FTIR and surface morphology were analysed to study the effect of geopolymer content. Water absorbency and adhesion strength of hybrid hydrogel were also investigated by varying the geopolymer content from 0.5 wt% to 2.5 wt%. Lastly, the anti-biofouling performance was done to determine the feasibility of hybrid hydrogel as an anti-biofouling coating.

2. Methodology

2.1 Materials

Fly ash was obtained from a power plant in Malaysia. The chemical composition of SiO₂ + Al₂O₃ + Fe₂O₃ of 78.58 wt%, SO₃ of 1.35 wt% and CaO of 9.84 wt% indicated that this was a Class F fly ash, as described in ASTM C618.

Acrylamide (AAM, 99 %), acrylic acid (AAC, 99 %) and polyethylene glycol as monomers, N,N'-methylenebis(acrylamide) (MBA, 99 %) as a cross-linker and sodium hydroxide (NaOH, 99 %) as the alkaline activator were supplied by Merck. Ammonium persulfate (APS, analytical reagent) as the initiator were supplied by R&M Chemicals. All chemicals were used without further purification.

2.2 Synthesis of coating

Synthesised poly(AAM-co-AAC/EG) hydrogel via free radical polymerisation was started with the naturalisation of AAC with sodium hydroxide (NaOH) solution. 20 g of AAC was diluted in 200 mL of distilled water in a beaker. Then, NaOH was added into the beaker, and the procedure was continued by the addition of 4 g of AAM into the solution. The solution was continuously stirred by using a magnetic stirrer for 30 min. After that, the solution was heated at 65 °C for 5 min and 0.01 g of MBA and 0.09 g of APS were added into the solution. The solution was continuously stirred at 65 °C for another 30 min. Subsequently, 0.6 g of polyethylene glycol, 0.01 g of MBA and 0.09 g of APS were added into the solution. The hydrogel was heated and continuously stirred for 4 h before being cooled at room temperature.

Geopolymer was synthesised by continuously mixing fly ash with 10 M of NaOH solution for 15 min at 550 rpm with the solid to liquid ratio 3:1. Hybrid hydrogel (HH) coating samples were prepared by mixing geopolymer with hydrogel at 550rpm by using an overhead stirrer for 10 min. Five samples were prepared by varying the total weight percent of geopolymer to hydrogel from 0.5 wt% to 2.5 wt% relative to the total weight of hydrogel. The samples were named as HH0.5, HH1.0, HH1.5, HH2.0 and HH2.5 corresponding to the total weight percent of geopolymer.

2.3 Characterization

2.3.1 Fourier Transform Infrared (FTIR)

The surface functional groups identification of blank hydrogel, geopolymer and hybrid hydrogel (HH1.0) was examined by using FTIR spectra (Perkin -Elmer Spectrum One, FTIR-frontier). The wavenumber range was 4,000 cm⁻¹– 500 cm⁻¹, scan number for per sample was 16 and wave resolution was 4 cm⁻¹. The hydrogel and

hybrid hydrogel were oven dried for 24 h at 60 °C. The samples disk was prepared by mixing and compressing the samples and KBr power.

2.3.2 Scanning Electron Microscope (SEM)

The microstructure and surface morphology of synthesised hydrogel and hybrid hydrogel were observed by a scanning electron microscope (SEM) at an accelerating voltage of 20 kV. Four oven dried samples, which were blank hydrogel (HH1.0, HH2.0 and HH2.5) were analysed on their surfaces to study the effect of geopolymers amount added onto the morphology.

2.4 Testing

2.4.1 Water absorbency

Initially, the dried coating samples were weighed (M_o). The samples were immersed in two different mediums which were distilled water and artificial seawater (3.5 wt% of sodium chloride (NaCl)) for 24 h. The swollen hydrogel mass was then weighed (M). For each sample, the swelling degree was calculated by using Eq(1).

$$\text{Water absorbency} = (M - M_o) / M_o \times 100\% \quad (1)$$

2.4.2 Adhesion strength test

The adhesion strength test was conducted for all prepared samples. It was performed by using Elcometer 108 pull-off adhesion tester in accordance to ASTM D 4541. The samples were coated on carbon steel plates. Then, the samples were oven dried at 60 °C for 4 h. The thickness of the dried hydrogel coating was ± 1.0 mm.

2.4.3 Anti-biofouling performance test

The anti-biofouling performance test was performed via immersion of hydrogel coating in an algae suspension for 24 h. Three samples were tested, namely blank hydrogel, HH2.0 and uncoated steel plate as the control. Blank hydrogel and HH2.0 were coated onto a carbon steel plate and oven dried at 60 °C for 4 h prior to immersion in algae, *Chlorella vulgaris* sp. suspension. The algae suspension was continuously stirred at room temperature throughout the testing. The anti-biofouling ability of the hydrogel coatings was analysed by calculating the algae frequency on the steel plate after the immersion by using the quadrant sampling technique. The coated steel plates were photographed before and after immersion. To estimate the algae frequency, image of the steel plate was digitally gridded according to the exact scale or measurement. The area of each grid was set at 5 mm by 5 mm. The algae frequency for each steel plate was calculated by using Eq(2).

$$\text{Algae frequency} = (\text{Number of quadrats with algae}) / (\text{Total number of quadrats}) \times 100\% \quad (2)$$

3. Results and discussion

3.1 Fourier Transform Infrared (FTIR)

The graphical results from the FTIR spectroscopy for the coating samples are shown in Figure 1. Each spectrum specifically characterises the respective sample.

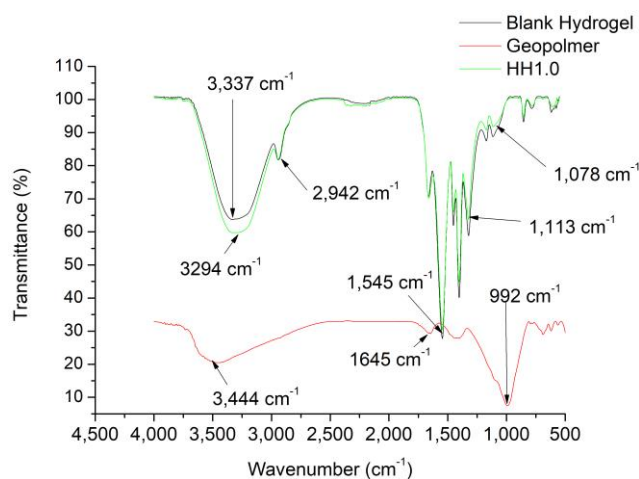


Figure 1: FTIR spectra of blank hydrogel, geopolimer and HH0.1

Based on the spectrum of the poly(AAm-co-AAc/EG), the blank hydrogel, the significant peaks were identified at the wavenumber of $3,337\text{ cm}^{-1}$ which indicated the presence of -OH and N-H bond stretching, at $2,942\text{ cm}^{-1}$ which indicated the presence of O-H bond stretching and $1,545\text{ cm}^{-1}$ which corresponded to C-O-C bond bending. The N-H bond and O-H bond verified the incorporation of the acrylamide and acrylic acid in the hydrogel network. Then, the C-O-C bond indicated that the polyethylene glycol molecular chains were introduced into the hydrogel network. The bonds proved the compatibility of acrylamide, acrylic acid and polyethylene glycol as the monomers of the poly(AAm-co-AAc/EG) hydrogel.

A significant peak of geopolymer spectrum was identified at the wavenumber of around 992 cm^{-1} . The absorption peak was attributed to the Si-O-Si or Al-O-Si asymmetric stretching mode. Significant broad bands were observed at wavenumber of $3,444\text{ cm}^{-1}$ and $1,645\text{ cm}^{-1}$ which indicated the presence of O-H stretching mode and O-H bending mode (Kramar and Ducman, 2015). The bonds appeared in the geopolymer as a result of the fly ash alkali activation by using sodium hydroxide (NaOH). The spectrum appeared similar to a previous research (Hamidi et al., 2016).

Meanwhile for spectra of HH1.0, the significant peaks were identified at the wavenumber of $3,294\text{ cm}^{-1}$, $2,946\text{ cm}^{-1}$, $1,545\text{ cm}^{-1}$ and $1,113\text{ cm}^{-1}$. The peaks corresponded to the N-H bond, O-H bond, C-O-C bond and Si-O-Si or Al-O-Si bond. The N-H bond and C-O-C bond represented the pure hydrogel sample in the coating. The Si-O-Si or Al-O-Si asymmetric stretching mode was identified at the wavenumber of $1,078\text{ cm}^{-1}$. The peaks of HH1.0 spectra which significantly shifted to lower intensities, as compared to the blank hydrogel, confirmed that existence of interaction between geopolymer and the hydrogel network and formed hybrid hydrogel.

3.2 Scanning Electron Microscope (SEM)

The relation between the weight percentages of geopolymer in the hybrid hydrogel coating was visually analysed by using SEM under magnification of 500x. Based on Figure 2, there was no visible microcrack on the blank hydrogel. It was concluded that the absence of the microcrack corresponded to the absence of geopolymer in the respective coating. For HH1.0 and HH2.0, there were visible microcracks on the surface due to the presence of geopolymer. The presence of microcracks was possibly due to the inhomogeneity of geopolymer in the hydrogel network. The microcracks also increased as weight percentage of geopolymer increased. These microcracks were insignificant towards the adhesion strength of HH1.0 and HH2.0. Cracks on HH2.5 were seen to be larger and deeper as compared to the other samples, which resulted in poor force distribution within the hybrid hydrogel chain and contributed to low adhesion strength.

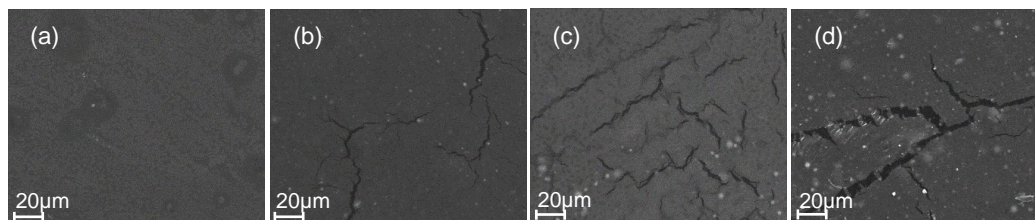
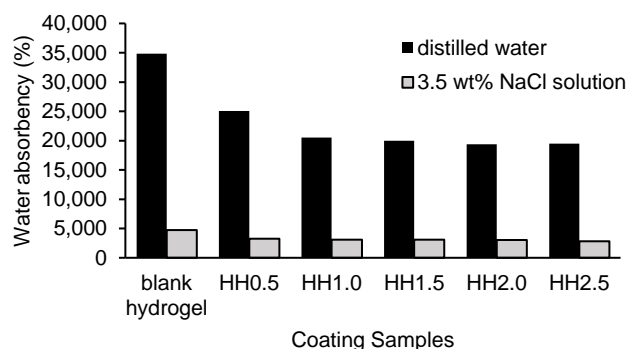


Figure 2: Surface morphology of (a) blank hydrogel, (b) HH1.0, (c) HH2.0 and (d) HH2.5 at magnification of 500X

3.3 Water absorbency

The water absorbency of blank hydrogel, HH0.5, HH1.0, HH1.5, HH2.0 and HHH2.5 in distilled water and artificial seawater (3.5 wt% NaCl solution) were compared and displayed in 3Error! Reference source not



found..

Figure 3: Water absorbency of coating in distilled water and 3.5 wt% NaCl solution (artificial sea water)

Based on the graph, it was concluded that the water absorbency of the hybrid hydrogel was significantly higher in distilled water than in artificial seawater. The difference in the water absorbency was due to the significant change in the osmotic pressure in the hydrogel. The osmotic pressure significantly decreased in the artificial seawater due to the high salt content in the solution and weak hydrogen bonding interaction of water molecules with the hydrogel samples (Huang et al., 2016). These resulted in lower water diffusion rate from the solution into the hydrogel coating. Both tests, in distilled water and artificial seawater, showed a drop in the swelling capacity when geopolymer was added. This was because the hydrophobic property possessed by the geopolymer network.

3.4 Adhesion strength

The adhesion strength of the coating on the steel plate was measured in the form of pressure by using Elcometer 108 pull-off adhesion tester, which is shown in Figure 4(a). The optimum weight percent of geopolymer to hydrogel was 2.0 wt%, which resulted in the highest adhesion strength of 6.5 MPa. The adhesion strength was proportionally increased to the amount of incorporated geopolymer. The adhesion enhancement by the geopolymer was associated with the formation of metal-oxygen-metal bonds between the geopolymer network and the metallic substrate (Yong et al., 2007).

The physical interaction between the geopolymer and the substrate surface also contributed to the improvement. In this case, Si-O-Fe and Al-O-Fe bonds were formed between the geopolymer in the hydrogel network and the steel plate, creating a strong connecting bridge between two materials. These strong metallic bonds improved the adhesion of the hydrogel coating (Yong et al., 2007). Therefore, more metallic bonds were formed with higher weight percentage of geopolymer, which increased the adhesion strength of coating. In terms of overall trend, the adhesion strength of coating increased as the weight percentage of geopolymer increased until it reached its optimum point. The adhesion strength of the hydrogel coating started to decrease when the percentage of geopolymer was more than 2.0 wt%. The drop in adhesion strength could be explained based on the surface morphology of coating. Based on the SEM results, the surface of HH2.5 had larger and deeper cracks as compared to HH1.0 and HH2.0. The cracks were no longer considered as micro-cracks as in HH1.0 and HH2.0. The presence of the relatively larger cracks was because the weight percentage of the geopolymer (2.5 wt%) in the hydrogel coating had exceeded the optimum range. The presence of cracks prevented the force from being evenly distributed in the matrices and caused a reduction in the adhesion strength. As the addition of geopolymer was beyond the optimum range (0 wt% to 2.0 wt%), incompatibility of the geopolymer with hydrogel network had overcome the adhesion enhancement via the metallic bonds.

3.5 Anti-biofouling performance test

Generally, high algae frequency indicates more deposition or attachment of the algae on the steel plate, which shows that the coating has low anti-biofouling ability. Based on Figure 4 (b), the algae frequency for the control sample was 26.19 % while the frequency for blank hydrogel was 1.02 % and HH2.0 was 2.04 %. It was concluded that the hydrogel coatings, with or without the addition of geopolymer, had significantly minimised the attachment of algae on the steel plate. Excellent performance of the hydrogel coating in preventing biofouling was closely linked to the high hydrophilicity of the coating (Wen-qi and Li-wei, 2017). A hydration barrier made of water molecules, was formed on the coating surface, repelling away the algae or biofoulants via a strong steric repulsion. The small difference in algae frequency between blank hydrogel and HH2.0 was due to hydrophobic property of the geopolymer.

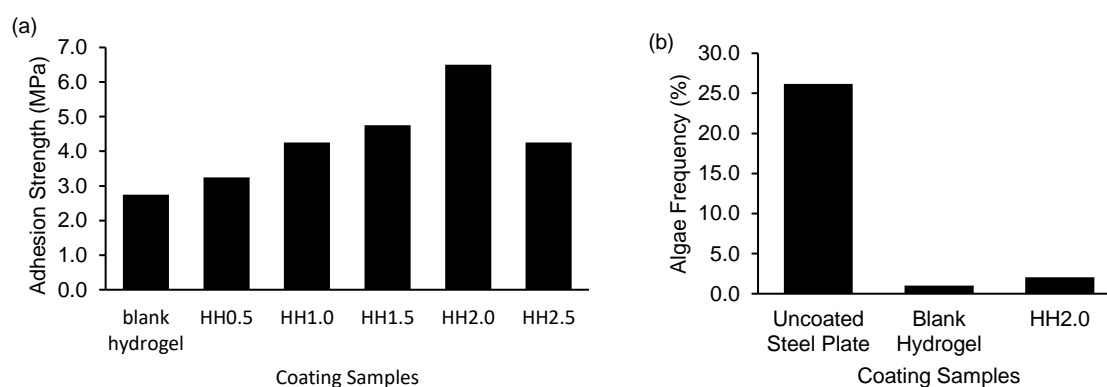


Figure 4: (a) adhesion strength of coating samples (b) algae frequency on surface of coating samples

4. Conclusions

Hybrid hydrogel coating has been synthesised by mixing poly(acrylamide-co-acrylic acid)/ polyethylene-glycol hydrogel with fly ash-based geopolymer. The significant FTIR peaks at wavenumbers of 3,294.35 cm^{-1} (N-H bond), 2,946.26 cm^{-1} (O-H bond), 1,545.13 cm^{-1} (C-O-C bond) and 1,112.87 cm^{-1} (Si-O-Si or Al-O-Si bond) indicated the copolymerisation of hybrid hydrogel. SEM results showed that the increase in geopolymer weight percent had caused more formation of cracks on the surface of coating. The water absorbency of the hydrogel coating in distilled water (up to 30,000 %) was significantly higher than in the artificial seawater (up to 5000 %) due to the decreased osmotic pressure in the hybrid hydrogel. It was found the hydrogel coating had significantly minimised the algae attachment on the steel plate. HH2.0 showed a reduction in the algae frequency by 92 % as compared to the uncoated steel plate. The addition of geopolymer had enhanced the hydrogel coating adhesion by up to 6.5 MPa as compared to blank hydrogel, which only had 2.75 MPa of adhesion strength on steel plate. Therefore, with the excellent anti-biofouling performance and highest adhesion strength, HH2.0 was selected as the optimum hydrogel coating in this work. It can also be concluded that fly ash-based geopolymer has potential to be used as a waste to wealth and is a more sustainable filler to increase the adhesion on substrate of anti-biofouling hydrogel coating.

For future works, the coating samples should be immersed in a more representative environment. The real condition of the seawater, including the aspects of microbial abundance, the temperature and the oceanic waves should be highly considered. To obtain more accurate results, the anti-biofouling test should be conducted in the real seawater. Next, the leaching rate of the monomers, such as polyethylene glycol from the hydrogel network, should be also studied. Although the hydrogel coating is environmentally friendly, the test is essential as the leaching rate affects the structural feature of the hydrogel coating and eventually decreases the efficiency of the anti-biofouling action.

Acknowledgments

The authors thank to the sponsor Yayasan Universiti Teknologi PETRONAS for the financial support under grant 0153AA-H47.

References

- Bodkhe R.B., Stafslie S.J., Daniels J., Cilz N., Muelhberg A. J., Thompson S.E.M., Callow M.E., Callow J.A., Webster D.C., 2015, Zwitterionic siloxane-polyurethane fouling-release coatings, *Progress in Organic Coating*, 78, 369-380.
- Fregolente P.B.L., Gonçalves H.L., Maciel M.R.W., Fregolente L.V., 2018, Swelling degree and diffusion parameters of Poly(Sodium acrylate-co-Acrylamide) hydrogel for removal of water content from biodiesel, *Chemical Engineering Transactions*, 65, 445-450.
- Gao Z., Duan L., Yang Y., Hu W., Gao G., 2018, Mussels-inspired tough hydrogels with self-repairing and tissue adhesion, *Applied Surface Science*, 427, 74-82.
- Hamidi R. M., Man Z., Azizli K. A., 2016, Concentration of NaOH and the effect on the properties of fly ash based geopolymer, *Procedia Engineering*, 148, 189-193.
- Huang K. T., Fang Y. L., Hsieh P. S., Li C. C., Dai N. T., Huang C. J., 2016, Zwitterionic nanocomposite hydrogels as effective wound dressings, *Journal of Materials Chemistry B*, 4(23), 4206-4215.
- Kramar S., Ducman V., 2015, Mechanical and Microstructural Characterization of Geopolymer Synthesized from Low Calcium Fly Ash, *Chemical Industry and Chemical Engineering Quarterly*, 21(1), 13-22.
- Nurioglu A. G., Esteves A. C. C., With G. De., 2015, Non-toxic, non-biocide-release antifouling coatings based on molecular structure design for marine applications, *Journal of Materials Chemistry B*, 3(32), 6547-6570.
- Taylor P., Schultz M. P., Bendick J. A., Holm E. R., Hertel W. M., 2011, Economic impact of biofouling on a naval surface ship, *Biofouling*, 27(1), 37-41.
- Telegdi J., Trif L., Romaszki L., 2016, Smart anti-biofouling composite coatings for naval applications, *Smart Composite Coatings and Membranes*, 123-155.
- Ueng T. H., Lyu S. J., Chu H. W., Lee H. H., Wang T. T., 2012, Adhesion at interface of geopolymer and cement mortar under compression: An experimental study, *Construction and Building Materials*, 35, 204-210.
- Wen-qi S., Li-wei Q., 2017, Synthesis of L-phenylalanine imprinted hydrogels with anti-biofouling capability by using a novel zwitterionic functional monomer, *Separation and Purification Technology*, 182, 247-254.
- Yang W., Lin P., Cheng D., Zhang L., Wu Y., Liu Y., Pei X., Zhou F., 2017, Contribution of charges in polyvinyl alcohol network to marine antifouling, *Applied Materials Interfaces*, 9(21), 18295-18304.
- Yong S. L., Feng D. W., Lukey G. C., Van Deventer J. S. J., 2007, Chemical characterisation of the steel-geopolymeric gel interface, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 302(1-3), 411-423.