Multifunctional Composites of Hydroxy-Fe/Polyacrylates and its Surface Properties

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Abstract. Multifunctional composites based on organic/inorganic materials had been synthesized using polyacrylate hydrogel as organic material and Fe(III)hydroxo as the inorganic material. These 2 materials were reacted to become a composite using two methods, chemically and physically. The composites did not dissolve in water when pH solution was changed, proving that they had high stability. However, physically-prepared composites still showed swelling properties whereas that of the chemically-prepared composites revealed very low swelling properties. Surface properties of the composites showed adsorption capability to cations and anions. Experiment result showed that the chemically synthesized composites had better adsorption for anions, however, the physically synthesized composites showed conversely. The analysis showed that adsorption of chemically synthesized composites followed the Langmuir isothermal model, meanwhile that of the physically synthesized composites followed the Freundlich isothermal model.

Keywords: adsorption, hydroxy-Fe/Polyacrylates, multifunction composites, swelling properties

1. Introduction

Water is an essential component of life for human, plant, and animal. Increasing of the human population will impact on the increasing need for clean water, food, and other things to support the needs of human life. Industrial wastewater is the most problem in the world because it will decrease the quality of clean water. The industrial revolution increasing the range of liquid waste that enters to the environment which are cationic or anionic but also organic compounds. Materials of ion exchange resins have been widely developed to overcome this problem. The ion-exchange resin is an insoluble phase which ions are bonded electrostatically. Ion exchange may occur when the resin is tangent to the solution having the same charge and it depends on the ion concentration and affinity in the solution[1].

The development of resin still focuses on degrading waste effectively and efficiently. Sabah *et al.*[2] reported that degradation of butyltin cation $((C_4H_9)_3Sn^+)$ waste from plastic industry in France can be overcome by aerobic biodegradation, while Orlando *et al.*[3] reported about the adsorption anion nitrate (NO_3^-) from agricultural waste through anion exchanger method using modified resin. In

fact, liquid waste that pollutes the environment is not only specific to one compound, so it needs a variety of methods and resin to degrade all wastewater into the environment. The development of new materials that can absorb and degrade liquid waste for anionic, cationic wastes and even organic compounds simultaneously will improve the efficiency of environmental management.

The modification of iron-polyacrylate biomaterial is aimed to make a new material that can adsorb cationic and anionic waste compound simultaneously. It is also used to reduce the cost of handling industrial waste. The use of polyacrylate as the main component is because it has the higher adsorption capacity[4], stable hydrogel phases, and inexpensive[5]. It has a potential carboxylic acid (-COOH) group which can adsorb cationic compound, while iron (Fe^{3+}) is used as a mixture to make the polyacrylate having cationic groups that can bind anionic compounds. According to Yetimoglu *et al.*[6], waste management can be solved by several methods, such as the formation of complexes, adsorption, precipitation, solvent extraction, and ion exchange. Adsorption method is used in this research because it is more efficient, cheaper, and easy to do. The adsorbent can also be regenerated and reused[7].

2. Experimental

2.1 Materials

Hydrogel (Sodium Polyacrylate) from Sumitomo Seika. $Fe(NO_3)_3.9H_2O$, HNO_3, $NaOH$, KH_2PO_4 and Methylene blue from Merck Company with pa. quality.

2.2 Methods

2.2.1 Synthesis of Composites. The composite synthesis was carried out with two Fe types, ie. Fe^{3+} and Fe polycation with several concentrations 0.025, 0.05, 0.075, and 0.1 M. Then 0.1 gram hydrogel was added to a beaker glass of distillate water until maximum limit of swelling. 15 mL solution of Fe^{3+} or Fe polycation was added into the beaker glass and stirred with a magnetic stirrer for 15 minutes. Then, NaOH solution was added to the mixture gradually until the pH in the range of 5 to 6 under stirring for 15 minutes. After that, the product was filtered using a vacuum and dried in the oven at 40 °C.

2.2.2 Anion Adsorption. The $H_2PO_4^-$ was used for adsorption anion. The analysis of PO_4^{3-} was carried out using molybdate-vanadate method. The adsorption experiment was prepared by adding a solution of $H_2PO_4^-$ various concentrations from 0 until 1400 ppm to 50 mg of composites and allowed to stand overnight. Then, 5 mL of the solution was transferred into the test tube for phosphate measurement. The solution measured its absorbance at a wavelength of 420 nm using a UV-Vis spectrophotometer. The data of the adsorption rate was calculated by adsorption capacity and analyzed by using Langmuir and Freundlich equations.

2.2.3 Cation Adsorption. The methylene blue was used for cation adsorption. Several concentrations of methylene blue from 0 to 700 ppm was added into 30 mg of the composite, then shaken and allowed to stand for 24 hours. After 24 hours, the supernatant was measured its absorbance at a wavelength of 664 nm. The determination of adsorption capacity on the adsorption data was done by Langmuir and Freundlich equations analysis.

3. Result and Discussion

The hydrogel used in this study were from polyacrylate polymers. Polyacrylate is a super adsorbent polymer which is a type of polymer that can absorb water as much as 100–1000 times the mass of polymers. This polyacrylate swelling process occurs through several stages. In the first stage, the water molecule will enter the most polar site of the polyacrilate matrix (hydrophilic group). Next, the hydrophobic group will interact with water. Crosslinks physically and covalently block the polyacrylate osmotic force against the solution so that the amount of water absorbed increases. The amount of adsorbed water between the polymer chains is increased until a bulk condition is obtained

[8]. The nature of the adsorption will be different when in solution there are dissolved ions such as $CaCl_2$ and ion Fe^{3+}. Both solutions can show that the ability of adsorption decreases with the presence of ion Ca^{2+} and Fe^{3+} ions (Fig. 1).
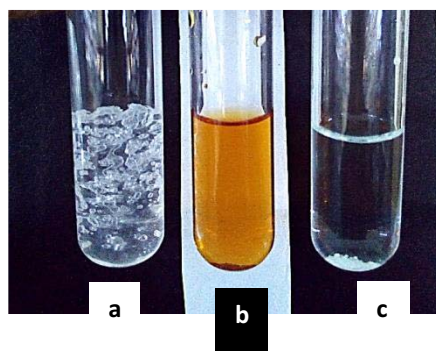
**Figure 1** The capability of polyacrylate to adsorb water (a), Fe^{3+} (b), and $CaCl_2$ solution (c)

This is because Ca^{2+} and Fe^{3+} ions will be ionically bound with carboxyl (-COO⁻) groups of polyacrylates thereby decreasing the amount of free hydrophobicity that can interact with water. This condition indicates that the increase in cation charge causes the polyacrylate deflating ability to decrease. If this ionic reaction occurs then it will cause the loss of the adsorption function of the material to be composite so that additional treatments are required in order to make the resulting composite still have an anionic and cationic active site. Preparation of biomaterial composite is made by two methods, namely the method of physical addition which is done by changing Fe in the form of polycation and then physically mixed with polyacrylate and chemical reaction done by adding Fe^{3+} ion into polyacrylate hydrogel. Both methods will produce powder-shaped biomaterials. The form of biomaterial powder has a larger surface area allowing for more interaction with the waste compound and can increase the reaction activity[9].

The physical mixing method is carried out by mixing polyacrilate with the Fe (III) hydroxo polycation. This polycation is first synthesized from Fe^{3+} which is reacted with NaOH then added to the polyacrilate. The polycation forming reaction consists of three stages, hydroxylation, olation and oxolation reactions. The hydroxylation reaction is a H_2O ligand replacement reaction of Fe (III) by the -OH ligand when the pH of the solution is increased due to the addition of NaOH. The formation of Fe (III) hydroxo complexes occurs rapidly because the bounded H_2O molecules are less stable. The high dynamic movement in the solution causes the emergence of a pranucleation cluster (PNC) reaction. During the PNC, there is an alternating reaction to the formation of several polycations connected by the -OH bridge (the olation reaction). However, the compound produced from this reaction is less stable to form another more stable compound. The conversion of the -OH bridge to the inter-Fe (III) bridge at the center of the gut (primary colloidal particles). This reaction is called the oxolation reaction. After that, there is a separation phase that is marked by the appearance of interface interaction. This interaction causes the aggregation of several polycations to form large aggregates (Fig. 2) [10–12].
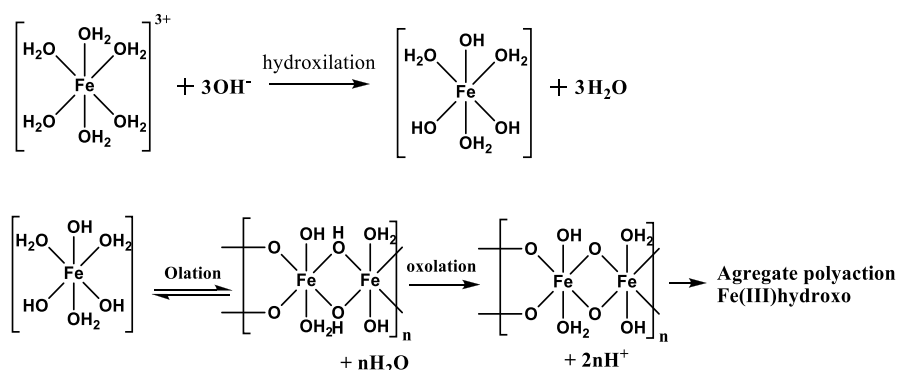
Figure 2 Mechanism of polycation synthesis reaction of Fe (III) hydroxo

The resulting polycation has an active site on the -OH_2^+ group attached to the central atom. The possible reaction is the interaction between -OH_2^+ group or Fe^{3+} and COO^- from the polyacrylate. This interaction can only take place on several sides of the active polyacrylate. (Fig. 3).
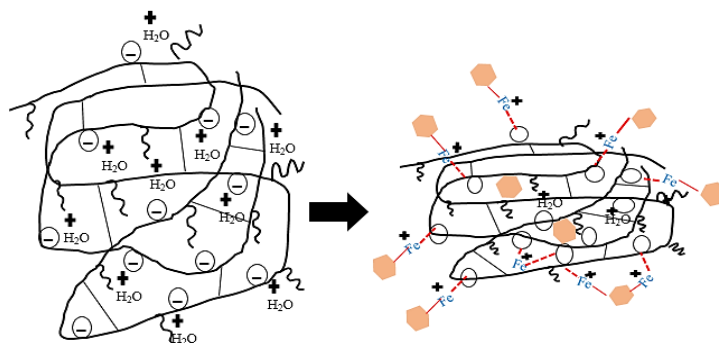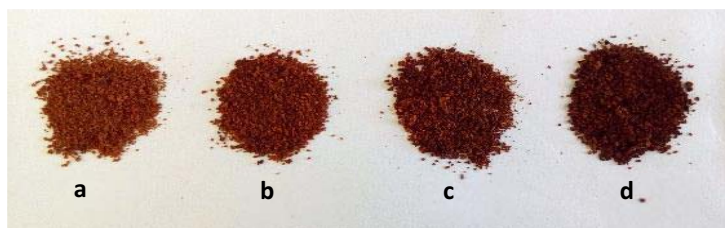

Figure 3 Illustration of the synthesis mechanism of the physical mixing composite: Fe (III) hydroxo ( ), Fe (-), and bond polyacrylates in polyacrylates (-)

This is due to the steric factor of the hydroxyl Fe(III) polycation having a large structure. In addition, a cross-linked polyacrylate shape can also reduce the likelihood of bonding on some active sites. This situation causes the agglomeration, which is the accumulation of particles into one molecule. The increase in Fe concentration causes the resulting composite color to be more dark brown (Fig 4). Unlike physical mixing, chemical reactions are done by mixing polyacrilate with Fe^{3+} ions or Fe(III)hydroxo polycation has not occurred. The resulting composite is brown with increasing intensity along with the increase in Fe^{3+} ions concentration used in synthesis (Fig 5).
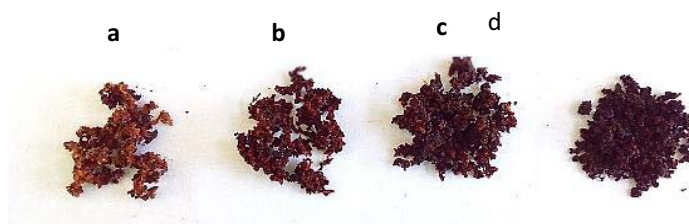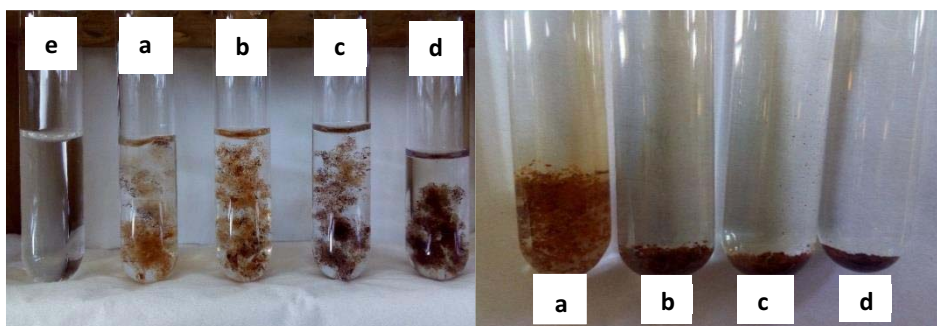

Figure 4 Composites of physical mixing at various concentrations of Fe (III) hydroxo: 0.025 M (a), 0.050 M (b), 0.075 M (c), and 0.100 M (d)

Figure 5 Composites of chemical reactions at various concentrations of Fe^{3+} 0.025 M (a), 0.050 M (b), 0.075 M (c), and 0.100 M (d)
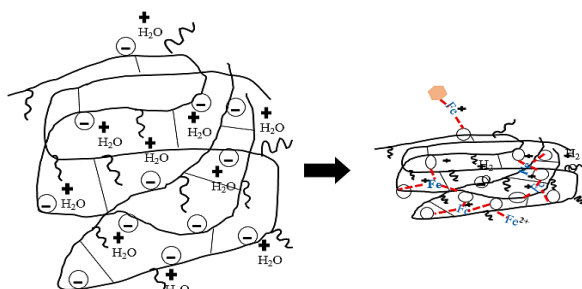
Figure 6 Illustration of the chemical reaction reaction composite synthesis mechanism: Fe (III) hydroxo (⬡), Fe (–), and bond polyacrylates in polyacrylates (-)

Figure 7 The stability of the physical mixing composite (left) and chemical reaction (right) at various concentrations of Fe (III) hydroxo: (a), 0.025 M (b), 0.050 M (c), 0.075 M (d), 0.100 M and blank (e)

This composite is produced likely powder. Ion Fe^{3+} are very small than Fe(III)hydroxo, it cause the interaction between the carboxyl (COO^-) group of polyacrylates and Fe^{3+} ion so avoid the steric effect. In addition, Fe^{3+} can bind with three carboxyl (COO^-) groups of polyacrylates at a time so that the polyacrylate further shrinks (Fig. 6). This shrinking causes the polyacrylate hydrogel to lose almost all its swelling capability. In addition to shrinkage, there are other assumptions during this reaction, namely the presence of hydroxylation, olation, and oxolation reactions. However, such reactions do not occur predominantly.

Composites produced either through chemical reactions or physical additions have high stability. This can be seen from the color of the unchanged solution after the composite is added and shaken strongly (Fig 7). This indicates that the iron is still bonded in the composite. Other physical properties observed in this study are composite swelling properties. The composite will swell when it absorbs water. Absorption ability of an adsorbent is expressed as the adsorption capacity. Large adsorption

capacity is expected from an adsorbent. The physically synthesized composite still has the ability to swell like its polyacrilate. This is because there is still an active side carboxyl (COO-) in the polyacrilate that does not interact with the polycation of Fe(III)hydroxo. This is evidenced by the observations showing that the composite still has a swelling capability (Fig 8). The swelling capacity decreases with increasing concentration of Fe(III)hydroxo polycation used. In chemical reaction composite, it has not swelling properties, because of carboxyl (COO$^-$) groups have interact bound with Fe3+ ion and it's reaction irreversible and makes a composite loss of swelling properties.

The composite will absorb the methylene blue as a cationic dye on the active side of the polyacrylate, via a free carboxyl group (COO$^-$), unbound to Fe(III). The active side will absorb the cation which is affected by the pH that should be optimum condition. In acidic solution, the active site will be protonated become -COOH thus reducing the adsorption ability of the methylene blue, whereas if the solution is basic condition then the active side will form -COO$^-$ that can be increasing the adsorption [13]. However, the composite will also be analyzed for its adsorption ability of phosphate anions via the active side –Fe(III) which may turn into Fe-OH in an alkaline atmosphere. Thus, in this study used pH 6–7 for analysis to optimize both active sides in absorbing the target compound.

The adsorption ability of an adsorbent can be known from its adsorbent capacity. The adsorption curve shows a significant increase in the early part of the curve. This can be understood by the concept that the increased concentration of adsorbate at adsorption causes the methylene blue cations that interact with the composite to increase so the methylene blue is absorbed. In addition, an increase in the initial concentration of adsorbate may also increase the cation diffusion into the composite due to the effect of the concentration gradient difference. This effect can cause the movement of cations to increase so as to accelerate the adsorption of cations by adsorbent [13].

The physically composite have adsorption capacity of the blue methylene with the concentration of Fe (III) ions 0.025 M and 0.100 M respectively yielded a capacity adsorption value of 958 and 416 mg/g and a composite with chemical composite of 208 and 54 mg/g (Fig 9). Composites with Fe (III) concentration of 0.025 M have the higher adsorption capacity than composite with Fe (III) concentration of 0.100 M. The active side of carboxyl group (COO$^-$) which absorbed the cation is bonded to Fe (III) to form the composite so the ability of binding methylene blue decreases, which results in a higher concentration of Fe (III) used, the less active side of the carboxyl (COO$^-$) group in the composite. In addition, significant differences are seen for both composites in absorbing the methylene blue cations. This is due to chemical composites of carboxyl groups (COO$^-$) of the polyacrylates bound to Fe^{3+} into the polyacrylate pores, which do not occur in physically mixing so its adsorption capacity to methylene blue decreases. However, the adsorption capacity of both types of composites is better when compared with the cypress leaves of 126.58 g/mg[14] and with tea waste of 85.16 mg/g[15].
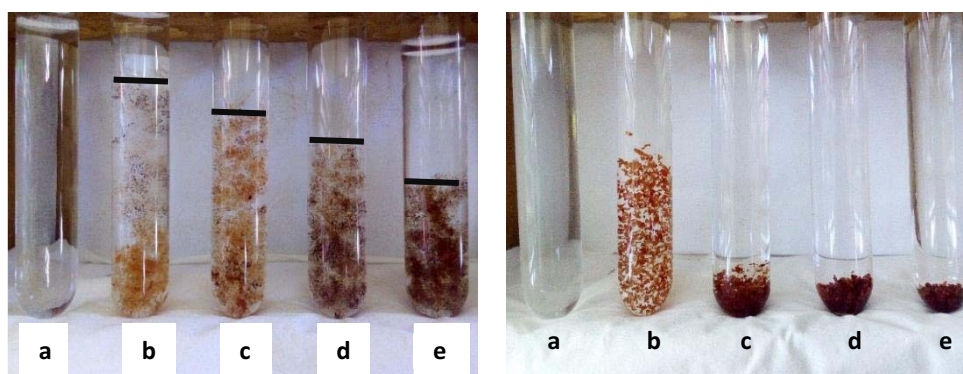

Figure 8 swelling properties of composite physically addition (Left) and chemical reaction (right) with blank (a), 0.025 M (b), 0.050 M (c), 0.075 M (d), and 0.100 M (e).
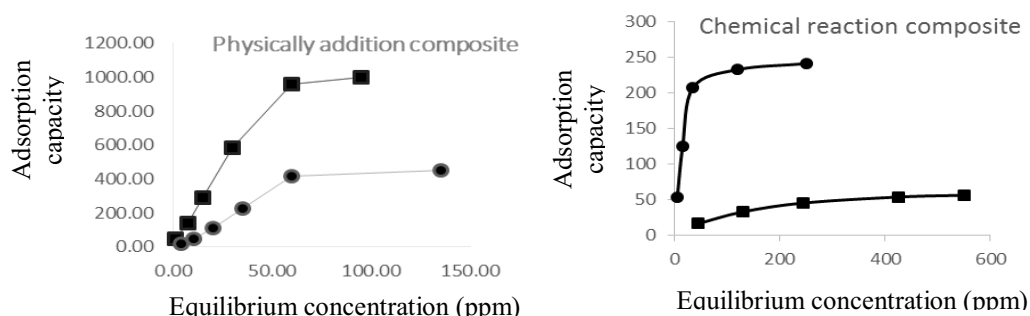
Figure 9 Cation adsorption capacity of physically composite (left) and chemical composite (right) of concentration Fe^{3+}: 0.025 M (●) and 0.100 M (■)

The Isothermal adsorption of physically composite following the Freundlich isothermal type based on the results indicated by the Freundlich isothermal linearity value is higher when compared with the linearity of Langmuir isothermal, that is 0.9812 and 0.9535 for the concentrations of 0.025 and 0.1 M respectively (Fig 10 and 11).
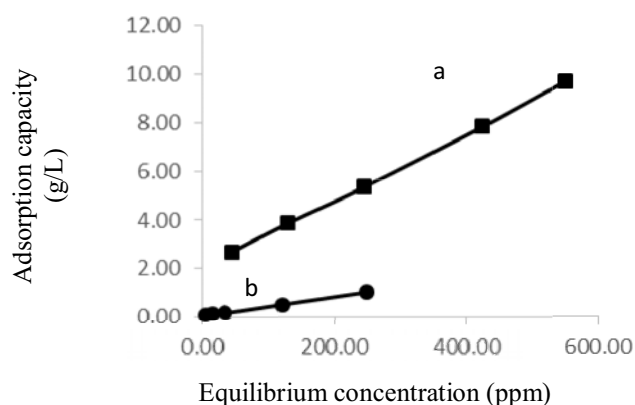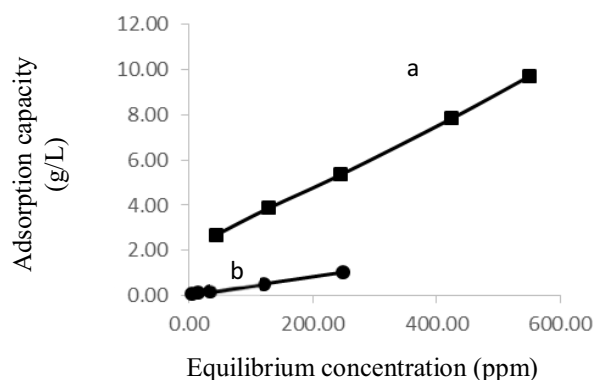

Figure 10 The Langmuir adsorption curve of the physical mixing composite at various concentrations of Fe (III) hydroxo: 0.025 M (●), 0.100 M (■), y = 0.0006x + 0.0338 (a), and y = 0.0006x + 0.1746 (b)
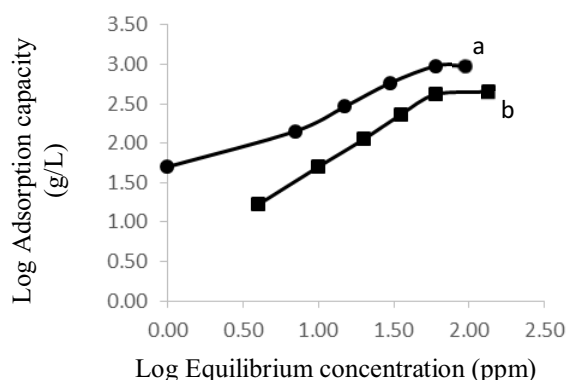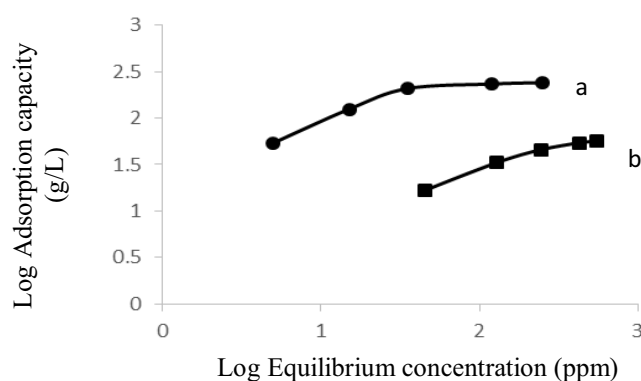

Figure 11 The Freundlich adsorption curve of the physical composite at various concentrations of Fe (III) hydroxo: 0.025 M (●), 0.100 M (■), y = 0.7073x + 1.6553 (a), and y = 1.0005x + 0.7076 (b)

The isothermal adsorption of composites chemically following the Langmuir isothermal model which has a higher linearity value of 0.9984 and 0.9994 when compared with the linearity of Freundlich isothermal (Fig 12 and 13).


Figure 12 The Langmuir adsorption curve of the chemical composite at various concentrations of Fe^{3+}: 0.025 M (●), 0.100 M (■), y=0.0138x + 2.0521 (a), and y=0.0039x + 0.0549 (b)

Figure 13 The Freundlich adsorption curve of the chemical composite at various concentrations of Fe^{3+}: 0.025 M (●), 0.100 M (■), y=0.3668x + 1.6009 (a), and y=0.4931x + 0.4421 (b)

The adsorption capacity of $H_2PO_4^-$ anion by physically composite with Fe(III) concentration of 0.025 M and 0.100 M were 75 and 100 mg/g, while chemical composite was 40 and 180 mg/g (Fig 14). The adsorption capacity of chemical composite was higher than physically composite. In this case, Fe (III) in chemical composite is spread uniformly on composite surfaces marked by composite color equalization. The presence of Fe (III) ions on the surface of the composite will maximize the adsorption of anions and have more interactions. In contrast to cationic adsorption, this anionic absorption involves the active side of Fe (III) so the greater the Fe (III) ions added in the composite, the increasing capacity of the adsorption. These results show much greater adsorption when compared with previous studies conducted[13] with an adsorption capacity of 3.5 mg/g using aluminum sludge adsorbent.
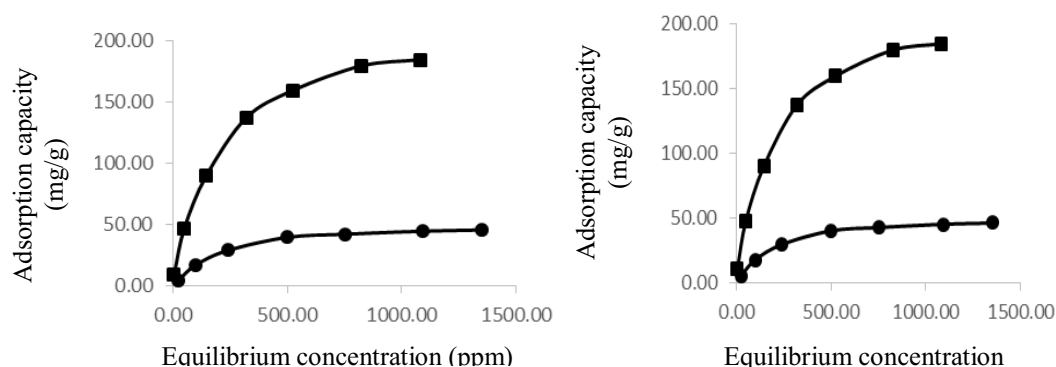
Figure 14 Anionic adsorption capacity of physically composite (left) and chemical composite (right) of concentration Fe^{3+}: 0.025 M (●) and 0.100 M (■)

The isothermal adsorption of the physically composite was demonstrated by higher Langmuir isothermal linearity when compared with Freundlich isothermal, ie 0.9935 and 0.9951 for concentrations of 0.025 and 0.1 M (Fig 15 and 16). This result is similar to previous research conducted[15] which also shows the isothermal type of adsorption. This approach assumes that the adsorbed anion forms a monolayer on the surface of the adsorbent, the adsorption is homogeneous across the surface of the adsorbent, and there is adsorbate adsorption being absorbed.
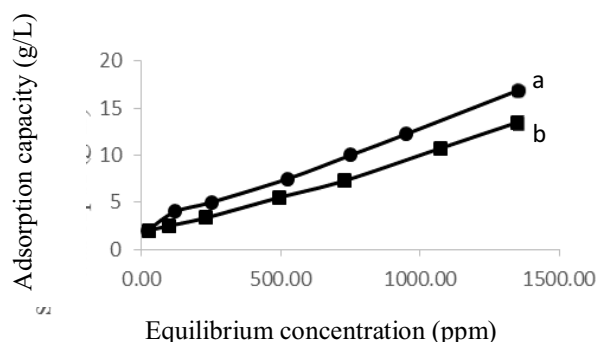
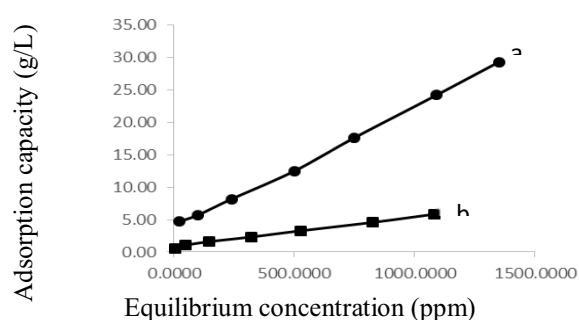

Figure 15 The Langmuir adsorption curve of the physical mixing composite at various concentrations of Fe(III)hydroxo: 0.025 M (●), 0.100 M (■), y=0.0108x + 2.1432 (a,) and y=0.0086x + 1.4783 (b)
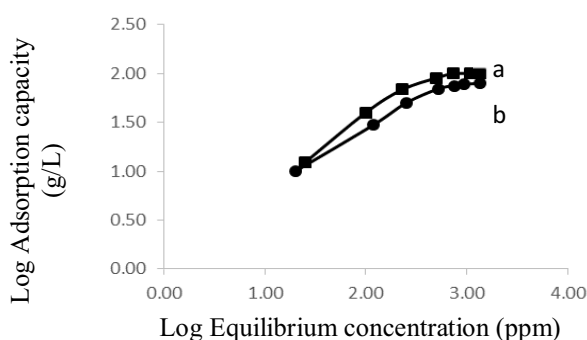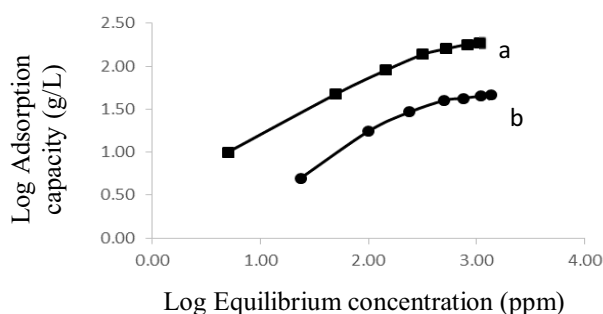

Figure 16 The Freundlich adsorption curve of the physical composite at various concentrations of Fe (III) hydroxo: 0.025 M (●), 0.100 M (■), y=0.5179x + 0.49 (a), and y=0.5115x + 0.3922 (b)

The determination of isothermal type performed on the analysis results showed that the anion adsorption by this type of composite follows Langmuir adsorption model. This is supported by Langmuir linearity values greater than Freundlich, ie 0.9985 and 0.9943 for concentrations of 0.025 and 0.100 M (Fig 17 and 18). This isothermal model is consistent with previous research conducted [13] which following the Langmuir isothermal model. These results assume that the adsorbed anions on the surface of the adsorbent also form an eclipse such as adsorption by a physical mixing composite. In addition, other assumptions also explain that the absorption occurring on all surfaces is homogeneous and adsorbate localization causes the adsorbate to not move to other parts of the adsorbent surface

Figure 17 The Langmuir adsorption curve of the chemical composite at various concentrations of Fe^{3+}: 0.025 M (●), 0.100 M (■), y=0.0187x + 3.7845 (a), and y=0.0047x + 0.7494 (b)

Figure 18 The Freundlich adsorption curve of the chemical composite at various concentrations of Fe^{3+}: 0.025 M (●), 0.100 M (■), y=0.5523x + 0.6866 (a), and y=0.5366x + 0.081 (b)

The implications of this research are aimed at agriculture and environment. The agricultural polyacrylate hydrogels can be used as water absorbers that can reduce waterlogging and soil erosion. Increased global temperatures caused many areas to experience severe drought. This hydrogel can help to keep the plants from lack of water and reduce the release of water for free. The addition of Fe compound into polyacrylate to form composite can be utilized as Fe source for plant. The use of composites in the environmental field, ie as adsorbents that doubles during its application. This provides benefits such as reduced costs, more efficient, and reduced time spent on interactions with target waste.

4. Conclusions

The hydroxy-Fe/Polyacrylate composite can be synthesized with two Fe sources, Fe^{3+} and Fe(III)hydroxo. The Fe(III)hydroxo based composite still has a heterogeneous surface and its surface is heterogeneous, whereas the composite synthesized with Fe^{3+} sources loses almost all its swelling and homogeneous surfaces. This affects the ability of composite adsorption to cations and anions. The analysis showed that the composites synthesized with Fe(III)hydroxo source could better absorb the

cation and follow Freundlich isothermal model. This is because the methylene blue is not only chemically adsorbed on the active composite side but also physically absorbed between the composite crosslinks. However, adsorbents with Fe^{3+} sources have a better ability to adsorb the anions and follow the Langmuir isothermal model. This is due to the homogeneous composite surface so that the occurrence of the occurrence is uniform across the composite surface.

References

[1]   Alexandrantos SD 2009 Ion exchange resins: a retrospective from industrial and engineering chemistry research *Ind. Eng. Chem. Res.* **48** 388–398

[2]   Sabah A, Bancon-Motigny C, Rodier C, Marchand P, Delpoux S, Ijjaali M and Tournoud MG 2016 Occurrence and removal of butyltin compound in a waste stabilisation pond of a domestic waste water treatment plant of a rural French town *Chemosphere* **144** 2497–2507

[3]   Orlando US, Baes AU, Nishijima W, and Okada M 2002 A new prosedure to produce lignocellulosic anion exchangers from agricultural waste material *Bioresour. Technol.* **83** 195–198

[4]   Tang Q, Wu J, Sun H, Fan S, Hu D, and Lin J 2009 Synthesis of polyacrylate/poly(ethylene glycol) hydrogel and its absorption properties for heavy metal ions and dye *Polym. Compos.* 1183–1189

[5]   Lin J, Tang Q, Wu J, and Hao S 2007 The synthesis and electrical conductivity of a polyacrylate/graphite hydrogel *React. Funct. Polym.* **67** 275–281

[6]   Yetimonglu EK, Kahraman MV, Ercan O, Akdemir ZS, and Apohan NK 2007 Nvinilpyrrolidone/acrylic acid/2-acrylamido-2-methylpropane sulfonic acid hydrogels: synthesis, characterization, and their application in the removal of heavy metals *React. Funct. Polym.* **67** 451–460

[7]   Samiey B, Cheng CH and Wu J 2014 Organic-inorganic hybrid polymers as adsorbents for removal of heavy metal ions from solutions: a review *Materials* **7** 673–726

[8]   Gibas I and Janik H 2010 Review: synthetic polymer hydrogels for biomedical applications *Chemistry and Chemical Technology* **4** 297–304

[9]   Rioux RM, Song H, Hoefelmeyer JD, Yang P, and Somorjai GA. 2005. High-surface-area catalyst design: synthesis, characterization, and reaction studies of platinum nanoparticles in mesoporous SBA-15 silica *J. Phys. Chem.* **109** 2192–2202

[10]   Bottero J, Manceau A, Villieras F and Tchoubar D 1994 Structure and mechanisms of formation of FeOOH(Cl) polymers *Langmuir* **10** 316–319

[11]   Sheck J, Wu B, Drechsler M, Rosenberg R, Driessche A, Stawski T and Gebaueur D 2016 The molecular mechanism of iron(III)oxide nucleation *J. Phys. Chem. Lett.* **7** 3123–3130

[12]   Rose A, Bligh M, Collins R, and Waite T 2016 Resolving early stages of homogenous iron(III) oxyhydroxide formation from iron(III) nitrate solutions at pH 3 using time-resolved SAXS *Langmuir* **30** 3548–3556

[13]   Yang Y, Zhao YQ, Babatunde AO, Wang L, Ren YX, and Han Y 2006 Characteristics and mechanisms of phosphate adsorption on dewatered alum sludge *Sep. Purif. Technol*. **51** 193–200.

[14]   Barros JLM, Macedo GR, Duarte MML, Silva EP, and Lobato AKCL 2003 Biosorption of cadmium using the fungus *Aspergillusniger Braz. J. Chem. Eng*. **20** 1–7

[15]   Yagub MT, Sen TK, and Ang HM 2012 Equilibrium, kinetics, and thermodynamics of methylene blue adsorption by pine tree leaves *Water, Air, and Soil Pollution* **223** 5267–5282.

[16]   Uddin MT, Islam MA, Mahmud S, and Rukanuzzaman M 2009 Adsorption removal of methylene blue by tea waste *J. Hazard Mater.* **164** 53–60