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Swelling kinetic behavior of biochar-*graft* superabsorbent polymer composites

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Abstract. Superabsorbent polymers (SAPs) are crosslinked three dimensional structures that poses high swelling capacity in aqueous medium. Its application in agriculture beneficial as it is able to retain moisture in soil. SAPs incorporated with bio-char have been prepared via solution polymerization of polyacrylic acid with co-monomer of polyacrylamide in the presence of bio-char using methylenebisacrylamide (MBA) as a crosslinking agent and ammonium persulfate (APS) as an initiator. In this research, the swelling kinetic behavior of SAP with biochar was studied on the effect of biochar percentage loading from 0-0.8wt. SEM imaging of sap incorporated biochar shows a porous structure which influences water absorbency. The maximum of water absorbency capacity reached an optimum value of 129.89 g/g at 0.4 % before decreasing with increasing bio-char loading. Mathematical model of kinetic diffusivity also revealed that the SAP-biochar incorporated follows a second order kinetic. The presence of bio-char could enhance physical properties by increasing the water-holding capacity, enhancing its water absorbency ability. Application of SAP incorporated biochar not only able to retain water, it could also help to fertilize agriculture.

1. Introduction

Superabsorbent polymers (SAPs) are hydrogels that contains three dimension polymeric chains, carrying dissociated, ionic functional groups. Their ability to absorb water or solvents multiple times its sizes makes it very useful in many applications [1]. The presence of hydrophilic groups such as carboxylic, carboxamide, hydroxyl, amine and amide in the polymer backbone are the main cause of the hydrophilic nature of SAPs [2]. Because of their ionic nature and interconnected structure, they absorb large quantities of water via hydrogen bonds, increasing the entropy of the network to make the SAPs swell dramatically in size. Application of SAPs, especially in agriculture is beneficial due to its ability to absorb and retain water [3]. This would benefit soils so as watering frequency can be reduced and soil moisture can be maintained especially in drought prone area.

SAPs that were incorporated with organic materials such as biochar received a fair amount of attention these recent years. These incorporated type of SAPs have the advantages of high hydrophilicity, sustainability, biodegradation properties and non-toxic base components which could lead to a much environmentally application [4]. Solution copolymerization of acrylic acid and acryl amide were commonly used in producing an environmental friendly hydrogel which could also achieve a high-water absorbency capacity. Ammonium persulfate (APS) as an initiator were often used with the presence of methylenebisacrylamide (MBA) as a crosslinker [5]. The application of SAPs with incorporation of biochars in agriculture offers some solutions that were faced by degraded



lands due to human activities and mother nature. Combination of SAPs and biochar are like 'artificial humus' as the SAPs are hydrophilic and contain carboxylic groups while biochars tends to be porous in nature which also helps in water retention [6]. These structures which both possessed enable them to bind cations and water, providing ways for water management. Several research studies points to their ability to increase the plant- available water in the soil, enabling it to survive longer with water shortage, increase soil fertility and agricultural yields [7].

SAPs and biochar induce a significantly higher growth rate in plants as it provides readily used carbon for the fertilization of soil, hence reducing the use of synthetic fertilizer [8]. Further research also proves that presence of biochar in soil also help in neutralizing the soil by binding with heavy metals and mitigate their action on plants as well as the effects of salinity [9]. The significant and novelty of this study is that corporation of SAP with fillers such as biochar will play a major role in the production of the higher performance SAPs in terms of water absorbency.

2. Materials and method

2.1. Materials

The main chemicals used for synthesizing the SAPs were acrylic acid (AA) as monomers with 99% of purity, acrylamide (AM) as co-monomers with 98.5% of purity, methylene bisacrylamide (MBA) with 99% of purity as crosslinker and ammonium persulphate (APS) with 98% of purity as the initiator. Sodium hydroxide (NaOH) with purity of 99% in pellets forms is used for the neutralization purpose. Biochar particles that were produced from Empty Fruit Bunch (EFB) via pyrolysis were used as filler for synthesis of SAPs-biochar composite.

2.2. Synthesis of SAPs –biochar composite

The synthesis of SAP was done through graft polymerization method, using acrylic acid (AA) and acrylamide (AAM) which acts as a monomer and co-monomer respectively. The two mixture solution was diluted with 60ml distilled water and further neutralized with NaOH in a 250 mL three neck flasks equipped with stirrer, condenser, nitrogen line and thermometer. 0.2% of biochar was later added followed by methylene bis acrylamide (MBA), which acts as a cross-linker agent in the solution and was stirred at room temperature until the MBA was completely dissolved. The flask then was immersed in a water bath and heated up to 70 °C and then APS initiator was added to the solution that was magnetically stirred at 300 rpm. The reaction mixture was left to stir for 2 hours until gel point before the resulting hydrogel was removed from the reaction and dried overnight in oven at 60 °C. The synthesis of SAP was repeated with 0.4%, 0.6% and 0.8% weight percentage of biochar. Controlled SAP without biochar as filler were also synthesized for comparison.

2.3. Water absorbency and swelling kinetic

The dried SAPs samples with constant weight were put into a beaker containing 100 mL distilled water. The sample was immersed in the distilled water for 6 hours in order to let the sample reach its swelling equilibrium. Every 5 minutes, the swollen sample was filtered by using a screen in order to remove the unabsorbed water. Water absorbency (WA) was calculated by using Equation 1 where M_0 and M_t represents weight of initial sample and weight swollen sample on given time [10].

$$WA = \frac{M_t - M_0}{M_0} \quad (1)$$

The swelling kinetic can be expressed as Equation 2:

$$\frac{dW}{dt} = K(W_\infty - W) \quad (2)$$

where W is the water content of the superabsorbent at time t and K is a constant.

2.4. Kinetic diffusivity

The kinetic of water diffusivity behavior of both samples were calculated using Equation 3 [11], where F stands for the diffusion mechanism of water in the hydrogel:

$$F = \frac{M_t}{M_\infty} = kt^n \quad (3)$$

where M_t and M_∞ are the amounts of solvent diffused into the hydrogel at time t and at equilibrium, respectively; k is the diffusion rate constant and n is the diffusion exponent which determines the type of diffusion mechanism as well. k and n stands for intercept and slope of the line value which can be obtained from the graph of $\ln F$ versus $\ln t$.

3. Results and discussion

3.1. Swelling kinetic study

Figure 1 shows the time dependencies of water absorbency behavior of different weight percentage of biochar filler. Observing from the graph trend, the absorption value of all the samples were increased tremendously at the beginning of swelling time and reached a maximum value at certain period. The swelling time for the samples to achieve maximum absorbency value increases as the amount of biochar percentage increased from 0% to 0.4%. However, the time taken for the sample to reach maximum swelling decreases as biochar percentage is increases at 0.6% and 0.8%. From this observation, it can be stated that the addition of carbonaceous particles improved the water absorbency of the samples but somehow reduce the absorbency rate as it required longer swelling time to achieve maximum absorption when the biochar percentage was increased above 0.4%.

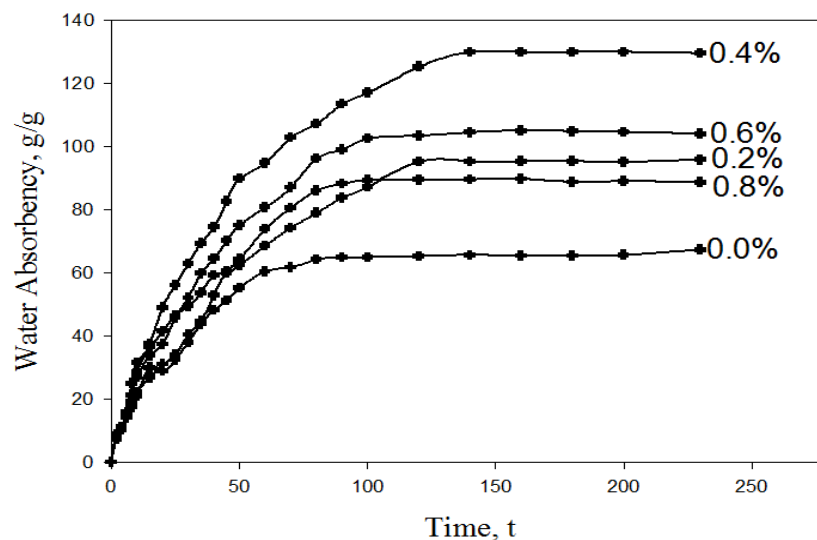


Figure 1. Time dependencies of water absorbency percentage of SAP with different filler percentage.

Figure 2 shows the SEM imaging of SAP incorporated biochar at 0.4% weight. Due to the porous nature of biochar, water is easily diffuse and binds on the porous surface of biochar as well as on the polymeric chains of SAPs, occupying the space. Hence, as biochar increases up to 0.4%, its swelling increases and the time for it to reach swelling equilibrium also increases. The decrease in both the swelling equilibrium and the time dependency on samples with biochar percentage at 0.6% and 0.8% was simply due to the increased density of polymeric chains. Maximum absorbency at 0.2% was higher compared to 0.8% which could be explained by the saturated crosslink network of the polymeric chains due to the amount of carbon present. The SAP incorporated with biochar at 0.8% is

more saturated compact compared to SAP of 0.2%, which minimizes the space for water diffusion to take place.

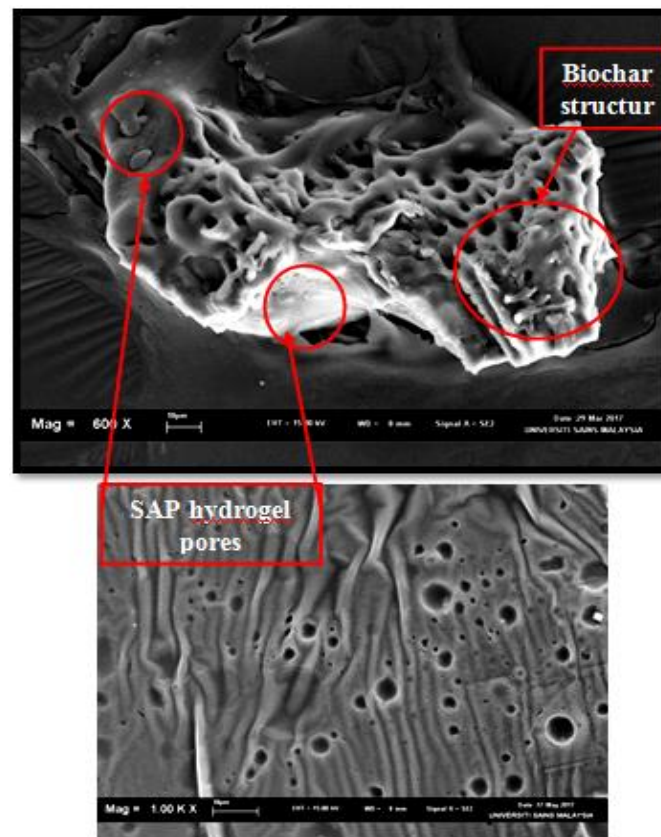


Figure 2. Surface morphology of SAPs incorporated biochar at 0.4 wt%.

In order to examine the controlling mechanisms of swelling processes, several kinetic models have been used to test experimental data. The swelling kinetics were analyzed in order to find out whether swelling follows first or second order kinetics [12]. For the first order kinetics, rate of swelling at any time is proportional to the water content before the equilibrium absorbed water (W_{∞}) has been reached. If the swelling process of superabsorbent follows a first order kinetics, the plot of the variation of $\ln (W_{\infty}-W/W_{\infty})$ as a function of time should give a straight line [13]. However, based on Figure 3, the swelling process of the superabsorbent polymer incorporated with biochar did not show a straight line hence, not follow a first order kinetics. Considering the second order kinetics, the swelling rate at any time may be expressed as Equation 4:

$$\frac{dW}{dt} = K(W_{\infty} - W)^2 \quad (4)$$

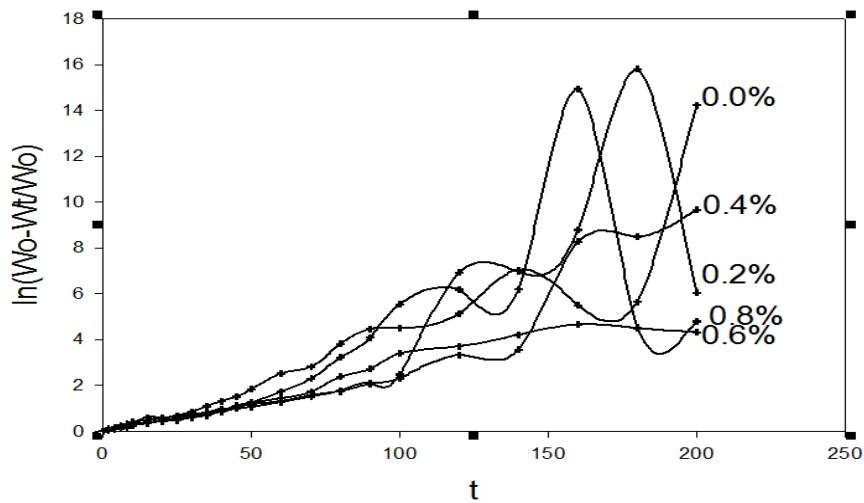


Figure 3. First order kinetic study of SAP different percentage biochar filler.

Integration of Equation 4 with the limits $t=0$ to t and $W=0$ to W and after rearrangement, the following equation is obtained:

$$\frac{t}{W} = \frac{1}{KW_{\infty}^2} + \frac{1}{W_{\infty}}t \quad (5)$$

It was found that swelling data of superabsorbent in water gives a straight line as observed in figure 4. Hence, the swelling of both SAPs with and without carbonaceous filler obeys second order kinetics.

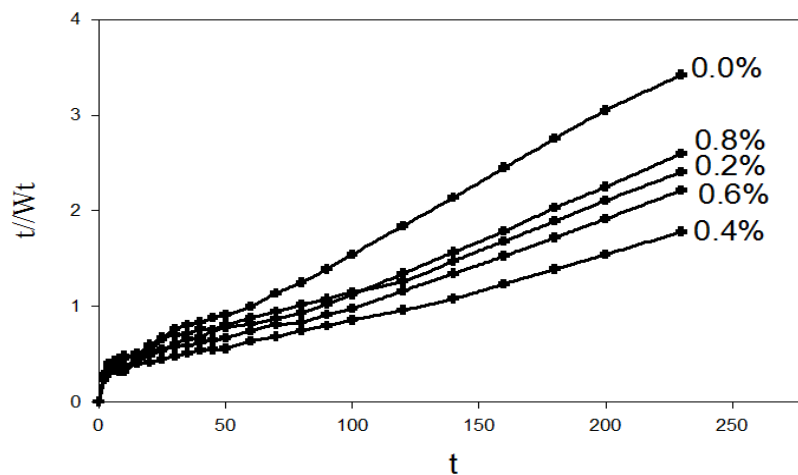


Figure 4. Second order kinetic study of SAP with different percentage biochar filler

3.2. Kinetic diffusivity study

Hydrogel can absorb water and expand multiple times its size. Diffusion involves migration of water into pre-existing or dynamically formed species between hydrogel chains [14]. Swelling of hydrogel involves larger scale segmental motion resulting increase in spaces between polymer chains. Plots of $\ln F$ versus $\ln t$ for SPCs could be seen in figure 5. The data obtained for absorbency at equilibrium and at time intervals were fitted in the Equation 2 to determine the value of n and k .

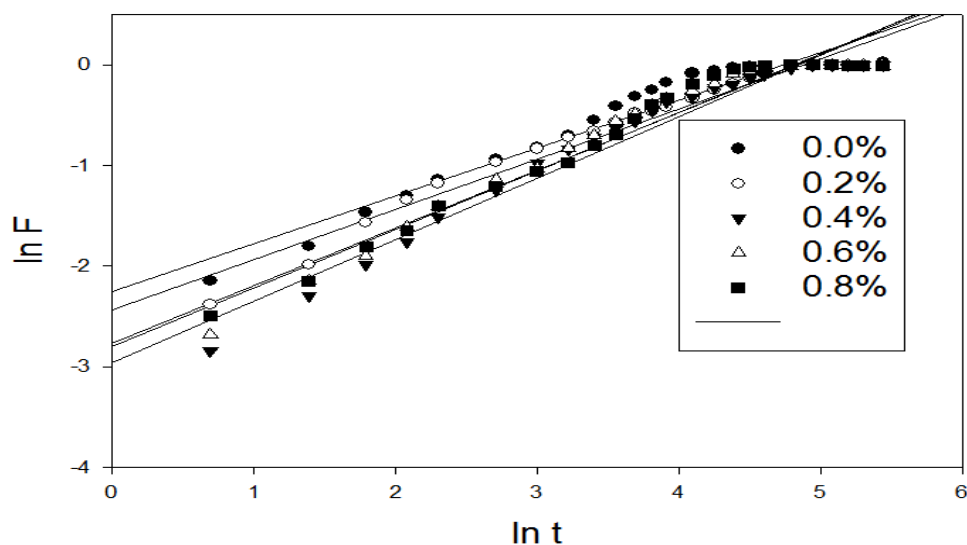


Figure 5. Plot of $\ln F$ versus $\ln t$ for SAP with different percentage of biochar filler.

The diffusion is characterized Fickian if $n < 0.50$ while in the case $0.50 < n < 1.00$, the diffusion is non-Fickian (anomalous) type. The n and k values depend on the absorbency behavior of the SAPs which were influenced by many factors. Based on table 1, it can be observed that both samples showed slightly non-Fickian behavior. Generally, when the diffusion is Fickian type, the water (solvents) absorbed by the SAP is relatively small and the possibility for polymer chain relaxation is seldom happened, but when it relaxes quickly, the swelling of SAP is controlled by the diffusion of water molecule into the network. When the diffusion mode shows anomalous behavior (non-fickian), the relaxation and diffusion time are of the same order of magnitude. Therefore, as the solvent diffuses into the hydrogel, there is delay in rearrangement (rupturing) within the polymer chains.

Table 1. Variation of n and k parameters of the superabsorbent polymer incorporation of different weight percentage of biochar.

Percentage Carbonaceous Loading, %	n	K
0.0	0.430	2.089
0.2	0.476	2.257
0.4	0.499	2.440
0.6	0.481	2.795
0.8	0.473	2.767

According to Zhao et al. [15], the increasing phenomenon of n value was a result from the entanglement and thermodynamic forces. Firstly, when n value increased, chain entanglement was also increased, hence reducing the space between different polymer chains. Secondly, strong thermodynamic forces which caused from high crosslinking density, makes water to diffuse faster. When this happened the time needed for water to diffuse in the whole network will also decrease hence resulting the increase in absorption rate.

The increase in k values suggests an increase in polymer-solvents interaction. The liquid flux rates through SAP are faster compared to SAP filled carbonaceous [7]. Presence of carbon in SAP forms crosslinking which increases mechanical strength and made the polymer "stiffer" compared to regular SAP. Therefore SAP without carbonaceous fillers is considered to be more flexible which enhances permeability [1]. This supports the study by Kamel et al. [16] which states that permeation rate for the molecules of similar shapes and chemical nature showed faster rates with decreasing chain length in polymeric materials.

4. Conclusion

In this study, the SAP sample containing different percentage of biochar filler was successfully synthesized via graft polymerization method. From the results, it can be concluded that the presence of biochar particles enhances the absorbency of the sample. Increased filler percentage results in higher water absorbency capacity, with the maximum value at 129 g/g at 0.4% biochar filler. Biochar are known for its porous structure which enables it to absorb and retain water molecules, hence slightly enhancing the water absorbency of SAP. Theoretically, biochar produces carbon particles that contribute to addition of functional groups which results to more ionic bonding when added as filler in SAP. However, as the biochar filler increased at 0.6% and 0.8% the maximum water absorbency decrease due to the saturated crosslink formation which leads to a more compact form that minimizes the space for water diffusion.

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