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Research Article

Combined Utilization of $KMNO_4$ Modified Starch Particles with Glycerol as De-Icer

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Öz

Nişasta ile modifiye edilmiş $KMnO_4$ (MS partikülü) ile gliserin çözeltisinden oluşan biyobozunur bir buz çözücü sistemi sunulan çalışma ile önerilmiş ve test edilmiştir. Deneyler değişen $KMnO_4$ (10, 15, 25%), MS partikül, gliserin % (20, 40, 60) ve çözücü miktarları (3, 6, 12 ml) ile gerçekleştirilmiştir. Çalışmanın temel hedefi gliserin ve $KMnO_4$ arasında ufak çaplı ekzotermik bir reaksiyonu tetiklemek ve reaksiyon sonucu açığa çıkan ısı ile buzun erimesini hızlandırmaktadır. Denemeler iki gruba ayrılmıştır. İlk olarak en yüksek sıcaklık artışını sağlayan en iyi koşullar istatistiksel olarak belirlenmiş ve buradan elde edilen sonuçların değerlendirilmesi ile buz çözme denemeleri gerçekleştirilmiştir. İstatistiksel analizler $KMnO_4$ ve MS partikül miktarlarının erime zamanının azaltılmasında birinci derecede rol aldığını göstermiştir. MS partikülleri ile gerçekleştirilen buz çözme denemelerinde kontrol sistemlerine göre erime zamanında azalmalar görülmüştür. Bu sonuç geleneksel gliserin bazlı buz çözücülere göre önerilen sistemin üstünlüğünü göstermektedir. MS partiküllerinin tekrarlı kullanımlarında erime zamanının kademeli olarak azalması çalışmanın en önemli sonucudur. Partiküllerin tekrarlı kullanımlarında artan bir performans sağlanması kayda değerdir. Sonuçlar aynı zamanda partiküllerin ekonomik olarak üretilebileceklerini göstermesi açısında da önem taşımaktadır.

Anahtar kelimeler: Nişasta, $KMnO_4$, Buz çözücü, gliserol, MS partikülü

Abstract

An alternative de-icer system consisted of biodegradable starch-modified $KMnO_4$ (MS), and glycerol solution was proposed and tested with the present study. Experiments were performed with varying $KMnO_4$ (10, 15, 25%) percentages, MS particle (0.06, 0.12, 0.24 g), glycerol (20, 40, 60%) and solution amounts (3, 6, 12 ml). The main idea was to induce a miniscule exothermic reaction between glycerol and $KMnO_4$ to enhance the melting of ice via heat release. The experiments were divided into two groups. Initially, the best conditions to yield the highest temperature increase was statistically determined, and de-icing experiments were conducted based on the interpretation of these results. Statistical analyses showed that the amount of $KMnO_4$ and MS had merely been responsible for maintaining an effective decrease in melting time. De-icing experiments conducted in the presence of MS particles indicated a decrease in melting time compared to control systems. This result indicated superior performance of the proposed system over traditional glycerol based de-icers. The higher decrease in melting time was observed in the presence of spent MS particles indicating their repetitive use and economically sound production.

Keywords: Starch,$KMnO_4$, de-icer, glycerol, MS particle

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1. Introduction

De-icer chemicals are frequently used in regions receiving high amounts of snow, and they are inevitable in maintaining the progress of daily life in winter. Various chemicals are used as de-icers based on the area of application. Glycerol is the main component of de-icer fluids used in aircraft and airport ground surfaces besides ethylene glycol (EG), propylene glycol (PG) and diethylene glycol which are among the significant chemicals in current use (Murphy *et.al.,* 2015). Bioaccumulation of these chemicals is not a problem as they can be degraded in relatively short time intervals. However, the problem is the increase in their population associated requirement, which results in very high chemical oxygen demand during their removal via degradation.

A separate discharge system is needed for the removal of glycerol and mentioned chemicals since the direct discharge of these chemicals will create additional problems in wastewater management (Murphy *et.al.,* 2015). On-site recycling and treatment of these wastes apart from wastewater are currently conducted by many airports located in Canada, United Kingdom, United States, Germany and Switzerland (Murphy *et.al.,* 2015; Johnson, 2012). Glycerol substitution is not possible as this chemical is already produced in large amounts as a side product in biodiesel production. The increasing utilization of glycerol is crucial to maintain an economically feasible biodiesel production (Simsek *et.al.,* 2016).

Besides the ones used in aircraft, a separate group of de-icer chemicals is currently being used in road de-icing. Sodium chloride, calcium chloride, and calcium acetate in solid form are used in vast amounts on the roads. Their use causes a high economic burden due to the increasing demand for material, equipment, and labour. These chemicals remain for long times on the road, and they have negative impacts on the bridges and other infrastructures (Ozgan *et.al.,* 2013). However, the major problem associated with their use is considered to be environmental rather than economic. Their harmful impacts on roadside vegetation and aquatic organisms have widely been investigated by various authors (Durickovic *et al.,* 2012; Mahros *et al.,* 2017;.Hintz and Relyea, 2017). Sodium chloride (NaCl) released during snow-melt has adverse effects on the growth and swim-up of Atlantic salmon, and it has also shown that their mortality increased in the presence of high salt concentrations (Mahros *et al.,* 2017). The growth ratios of rainbow trout (*Oncorhynchus mykiss*) exposured to $MgCl_2$, NaCl, and $CaCl_2$ were also investigated, and the results confirmed the decrease in growth of rainbow trout in the presence of NaCl and $CaCl_2$ in high concentrations (Hintz and Relyea, 2017). The direct and indirect effects of NaCl and the mixture of NaCl, KCl, $MgCl_2$ salts on freshwater organisms were shown in another study (Jones *et al.,* 2017). In a study by Jones et al., (Jones *et al.,* 2017) in the freshwater source containing periphyton, phytoplankton, zooplankton, American toads (*Anaxyrus americanus*) and wood frogs (*Lithobates sylvaticus*) a high NaCl (780 mg Cl^{-1}/L) concentration caused a marked decrease in the survival of wood frogs before and during metamorphosis and toad activity. Another study on living ecosystem also report a decline in urban trees as a result of the salt application in de-icing. The decrease was said to be due to the gradual increase of pH and electron conductivity of the soils located close to roads (Equizaa *et.al.,* 2017). Apart from the effects on land, these salts, especially sodium chloride, also affect the concentration of particulate matter in the atmosphere via suspension after drying of the road surface. Studies indicated that the contribution of salts as particulate matter concentration to atmosphere had similar values with particulate matter concentration during winter (Denby *et.al.,* 2016).

Literature studies indicate that chlorine content is mainly responsible for the harm done to the environment and therefore over years an increasing amount of investigations has been focused on producing alternative chlorine free de-icers (Yang and Montgomery, 2003; Fu and Mathews, 2005; Jin *et al.,* 2010; Oh *et al.,* 2017). Corn steep water, a by-product of corn wet milling, was utilized as a reactant to get biodegradable organic salts, and the advantage of this de-icer solution was stated to be free of chloride or inorganic acid salts used in production (Yang and Montgomery, 2003). Calcium combined with magnesium acetate (CMA) was used as road de-icer in another study. Fu and Mathews (Fu and Mathews, 2005) proposed an alternative and economic pathway for CMA production by fermentation and extraction of cheese whey instead of the current process conducted by the reaction of glacial acetic acid and limestone. Acetic acid utilized in calcium acetate production can be obtained from vegetable wastes by a two-step process. The produced acetic acid can be separated and purified by electro dialysis and reverse osmosis (Jin *et al.,* 2010). Biomass utilization to produce CMA as precursor was extensively investigated by the pyrolysis of corncob, palm kernel shell, and radiate pine to yield bio-oil at 430°C. CMA production was achieved by the reaction of acetic acid fractions obtained from their distillation and natural and calcined dolomite. The results indicated that calcined dolomite was better reactant than natural dolomite in CMA production (Oh *et al.,* 2017).

In the present study, an eco-friendly salt-based de-icer is proposed. The authors developed a de-icer containing two ingredients. The first ingredient was solid obtained by modification of starch with KMnO4 addition (MS particles). The de-icing effect was achieved by the reaction of these MS particles with a glycerol solution, the second ingredient of de-icer. Our approach towards de-icer production is somewhat different from those in literature. Based on the literature survey, it was our understanding that the materials used in de-icing were meant to decrease the freezing point of the surface of utilization and prevent the formation of ice on the structure. However, starting a minuscule chemical reaction on the surface of the ice with a combination of right components was not studied based on our investigations. The main idea is to create a highly exothermic reaction on the surface of the ice enabling the acceleration of its melting via temperature increase and preventing the reappearance of ice due to the heat released during reaction for a specified period. Synthesis of starch modified with KMnO4 was initially conducted to reach this goal, and glycerol solution in varying concentrations was added to this material to initiate oxidation reaction. Usually the oxidation of $KMnO_4$ in high amounts with glycerol results in the fire with the ash, CO_2 and H_2O formed during the process. However, the authors reacted solutions of glycerol with low quantities of $KMnO_4$ to prevent this type of incident but enable consumption of glycerol at the same time. The authors maintain that the harm emanated from chlorine deposition in nature could be reduced by the future application of this alternative de-icing system.

Starch is a well-known biodegradable and nontoxic polymer which exists in nature. The main advantage of this polymer is the ease of fabrication with the addition of various components (Namazi and Dadkhah, 2010). It has many applications depending on the use and treatment process (Bai *et.al.,* 2013; Poorgholya *et.al.,* 2017; Sarka and Dvoracek, 2017; Zhu, 2017). In de-icer applications, organic acids produced by hydrolysis of starch is further reacted with carbonate salts to produce de-icers (Jin *et al.,* 2010; Ganjal *et.al.,* 2007; Huo *et.al.,* 2005). Starch use as support material in a de-icing system was not previously investigated based on our literature survey, and an alternative method of starch as a de-icing component was introduced with the present study.

2. Materials and Methods

2.1. Synthesis of Starch Modified with $KMnO_4$

Synthesis of starch modified with $KMnO_4$ (MS) was the initial step of the study. A modified (Bai *et.al.*, 2013) procedure was developed for synthesis. The steps were given below:

- 1 g of soluble extra pure starch (Merck) and varying amounts of (%10, 15 and 25% of starch) $KMnO_4$ (Merck) was mixed with 20 ml of deionized water and homogenized at 5000 rpm for 1 minute.
- The solution was heated at 80°C for 1 hour. The temperature of the solution was kept constant by using a reflux condenser.
- The obtained solution was cooled down to 50°C by dropwise ethanol addition. 1ml ethanol/min for a total of 20 minutes was added to the solution to reach the required temperature and prevent starch solubilization.
- The resulting solution was centrifuged at 4000 rpm, and the remaining solid was obtained by freeze-drying (12 hours).

2.2. Characterization of MS particles

XRD and SEM analyses were conducted on MS particles to determine the structure of the solid and to validate the presence of MnO_2 on the structure. The X-ray diffraction (XRD) patterns were obtained by a Panalytical Empyrean instrument (λ= 1.5418 Å) at 200 kV and 50 mA in the range of 2Θ value between 5° and 80° with a speed of 10° min^{-1}. The surface morphology of microspheres was determined using an SEM, Zeiss Supra 40V device.

2.3. Experimental Studies and Statistical Analysis

As previously mentioned, varying amounts of KMnO4 were added to starch during synthesis. Besides $KMnO_4$ amount, various parameters such as total amount of MS particles, glycerol content in the solution, and the amount of glycerol solution used in the reaction were also be investigated. However, studying all of these parameters requires a high number of experimental work. This problem was solved by applying response surface methodology to determine the number and the order of experimental runs. The experiments conducted in this work were illustrated in Table 1. "A" corresponded to KMnO4 amount inside the starch. The amounts were determined as 0.1,015 and 0.25, with 0.15 being the centre (0). These values corresponded to 10, 15 and 25% of 1g starch. B is the amount of MS particles utilized in reaction. Its quantity was varied as 0.06, 0.12, and 0.24g with 0.12 being the centre (0). Finally, C is the amount of glycerol % in solution. Glycerol content was determined as 20, 40, and 60% with 40% being the centre (0). Another set of experiments with varying amounts of glycerol solutions (3, 6, and 12 ml) was also conducted. However, preliminary evaluation of results indicated a negligible effect of solution amount on temperature increase, and ANOVA was only applied to the results obtained with 6 ml of 20, 40, and 60% glycerol solutions. The results of all experiments in terms of temperature increase with varying KMnO4, MS amounts, the volume of solution and glycerol content in solution were illustrated in Supplementary file.

2.4. De-icing performance of pure and used MS particles on varying ice amounts

De-icing experiments were conducted at 4 and -16°C with different amounts of ice to imitate the effect of actual conditions. The parameters used in these experiments (e.g., the amount of $KMnO_4$ in MS particle, the amount of glycerol% in solution and the amount of MS particle) were determined based on the results of variance analyses. Additional experiments were conducted with only glycerol used as a de-icing chemical to validate supremacy of MS particles compared to glycerol.

Once MS particles are placed on the road or sidewalks, subsequent glycerol addition can be applied to these particles to enable complete snowmelt. This condition, which requires reuse of MS particles, was simulated with de-icing experiments with varying ice amounts (g) at varying temperatures. In these experiments, the ice after complete melting was removed from the holders and the same amount of ice was placed inside while no additional treatment (eq. washing, drying, etc.) was conducted to MS particles. The aim here was to determine the activity loss of MS particles in consecutive utilization. The experiments conducted in this section was given as a summary in Table 2. The experiments conducted with the sole utilization of 20 and 40 %glycerol was not given in Table 2 to prevent confusion. The related results, however, were interpreted in accordance on the "Results and Discussion" section.

3. Results and Discussion

3.1. Characterization of MS particles

XRD analyses of MS particles with 10, 15, and 25% $KMnO_4$ loading amounts were illustrated in Figure 1. XRD analyses were conducted to determine a possible reaction between $KMNO_4$ and starch during synthesis. This reaction occurring during synthesis could result in the loss of $KMnO_4$ prior to its use in de-icing. The most facile way to determine the possibility of starch oxidation was to validate MnO_2 presence in MS particles. Starch oxidation by $KMnO_4$ could take place either in acidic or alkaline conditions. Acidic conditions required the presence of sulfuric acid and 2h of reactions while alkaline conditions could be achieved via sodium hydroxide addition (Hebeish *et.al.*, 1999). In the present study, pH values of solutions were kept at neutral conditions during synthesis to avoid starch oxidation. 10 and 15% loadings revealed a little formation of MnO2, however, (111) and (021) crystal planes of MnO_2 were visible at 2Θ values of 37 and 66° in the case of 25% loading (Tian *et.al.*, 2017). Consequently, this loading value was determined as the threshold for $KMnO_4$ in MS particle. SEM image of MS particle with 10% $KMnO_4$ addition indicated the irregular formation of starch molecules with smooth surfaces with no detectable sign of cleavage (Figure 2) (Jan *et.al.*, 2017).

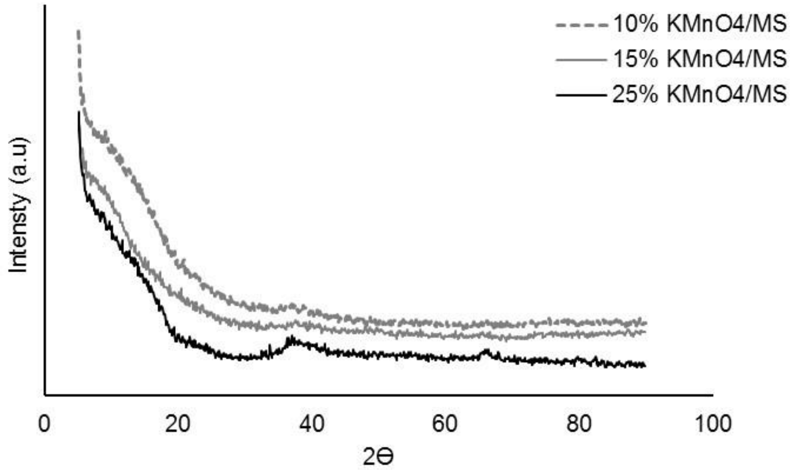

Figure 1. XRD analyses of MS particles.

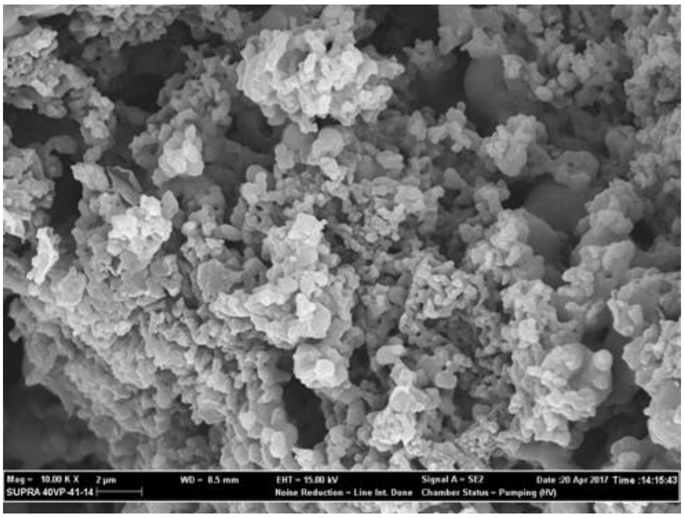

Figure 2. SEM image of MS particles with 10% $KMnO_4$ loading.

3.2. Reaction Experiments and Statistical Analysis

Combustion reaction between glycerol and potassium permanganate proceeds slowly at first. However, the rate of reaction increases as the reaction proceeds and consequently, a large amount of heat could be generated to enable temperature increase in the area of application. The main idea was to use $KMnO_4$ containing MS particles in ice and react these with glycerol. The heat generated during the reaction would melt the ice. Although the complete mechanism of this combustion reaction was not known, end products besides CO_2, H_2O and organic compounds contained K_2CO_3, Mn_2O_3, along with K_2MnO_4 and MnO_2 depending on the presence of water in the reaction medium. These compounds are known to induce plant growth. Moreover, utilization of MS particles with glycerol would reverse the harmful impacts on roadside vegetation and aquatic organisms emanated from salt utilization as de-icer.

Results of reaction experiments were given in Supplementary file, as previously mentioned. Analysis of variance conducted with selected results was illustrated in Table 3. Response model equation was determined as:

$$Y = 1.24091 - 0.75A - 1.5B - 0.15C + 1.77273A^2 + 1.55273B^2 - 0.727273C^2 - 0.625AB + 0.25AC - 0.125BC \quad (1)$$

Squared and adjusted square R values validated that the results had been statistically significant. The *p* values of A, B, A^2, $B^{2,}$ and AB were smaller than 0.05, showing that the obtained temperature increase was merely dependent on the amount of $KMnO_4$ and MS particle. On the other hand, the effect of glycerol % in solution was ineffective, as seen from the table. Response surface plot indicating the effects of MS and $KMnO_4$ amounts on temperature change was given in Figure 3. Temperature increase was highest either in the presence of highest $KMnO_4$ loaded in lowest amount of MS particle or in the presence of lowest $KMnO_4$ loaded in highest amount of MS particle. The opposite trend obtained for two parameters was among the highlights of study indicating combined effect of glycerol. It was thought that glycerol had both contributed as a de-icer itself and as a reactant in the reaction. This double effect also explained statistically insignificant values obtained with altered glycerol amounts. The safest environmental option, in our opinion, was selected with lowest amount of $KMnO_4$, highest amount of MS particle (0.24g) based on the results.

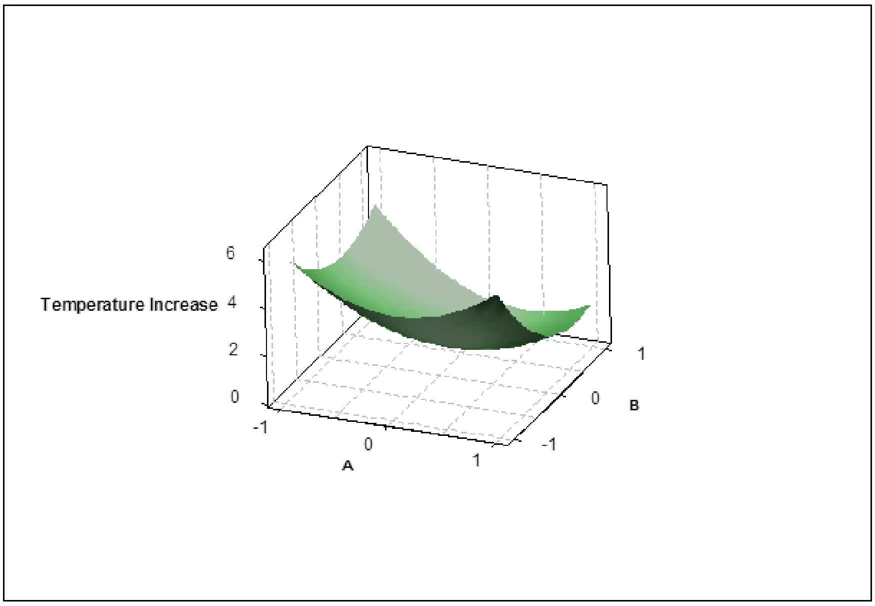

Figure 3. Response surface plots indicating the effect of KMnO4 amount in the particle and total amount of MS particle utilized for deicing. The plot was obtained based on center conditions of glycerol amount (40% glycerol) (A: Amount of KMnO4 inside MS particle; B: Amount of MS particle used in reaction)

Determination of de-icing performance of pure and used MS particles on varying ice amounts

Effect of glycerol amount on de-icing performance was investigated with 20 and 40% glycerol at -16 and +4°C, in the presence of 0.24g MS particles containing 10% $KMnO_4$ in its structure. At -16°C, the amount of glycerol did not affect melting time (Figure 4a) On the other hand, at +4°C, results indicated lower de-icing times with 20% glycerol. This result was important as glycerol could also be used as de-icer fluid, and its increased amount in the solution should be more effective in decreasing the melting time of ice. Based on the results obtained with lower amounts of glycerol at +4°C, our understanding was that the exothermic reaction between $KMnO_4$ in MS particle and glycerol had been more important in the formation of de-icing effect than sole utilization of glycerol. The better results obtained in lower glycerol amounts could be explained by higher diffusion of 20% glycerol solution inside MS particle due to its lower viscosity compared to 40% glycerol solution (Figure 4b). De-icing experiments at +4°C was also conducted with control in which the average melting time of ice was measured, and results indicated the high activity of MS particle and glycerol system in de-icing (Figure 4b).

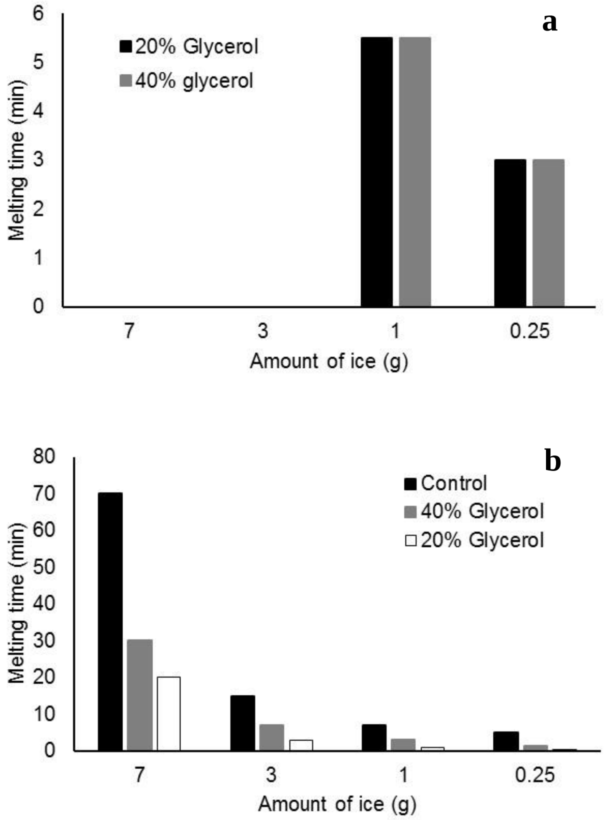

Figure 4. Effect of glycerol content in deicing performance at a) -16°C and b) +4°C (MS particle: 0.24g; $KMnO_4$%:10)

Additional experiments in the presence of glycerol was conducted without the use of MS particles in order to validate the effect of MS particle. Results were illustrated for both temperatures (-16 and +4°C) in Figure 5. Single use of glycerol was effective in decreasing the melting time of ice, as expected. However, lower melting time in the presence of MS particles was obtained, which revealed relatively higher performance as a de-icer.

Spent MS particles were used in de-icing experiments to determine their effect on repeated utilization. De-icing tests were performed with varying ice amounts at +4°C with 20 and 40% glycerol. As previously mentioned, 0.24g MS particles containing 10% $KMnO_4$ were utilized in all experiments. In the case of lowest ice amount, the particles were active until the 5th run with melting times being in close range. However, after the 5th run, an increase in melting time for both solutions was observed as seen in figure (Figure 6a). The increase in ice amount had an increasing effect on the melting time (Figure 6b), however, further growth in ice amount resulted in a decrease of melting time in repeated runs for both solutions. This is the most important result obtained in this study since it has not only showed that repeated use of MS particles had been possible but also a decrease in melting time could have been achieved in repeated use. The decline in melting time was thought to be due to the amount of water released during melting. We believe that a threshold value of ice enabling dissolution of starch existed. Although starch is not soluble in cold water, elevated amounts of water could result in some loss of starch. This enhanced accessibility of glycerol to $KMnO_4$ inside the structure, increasing the temperature and hence decreasing melting time.

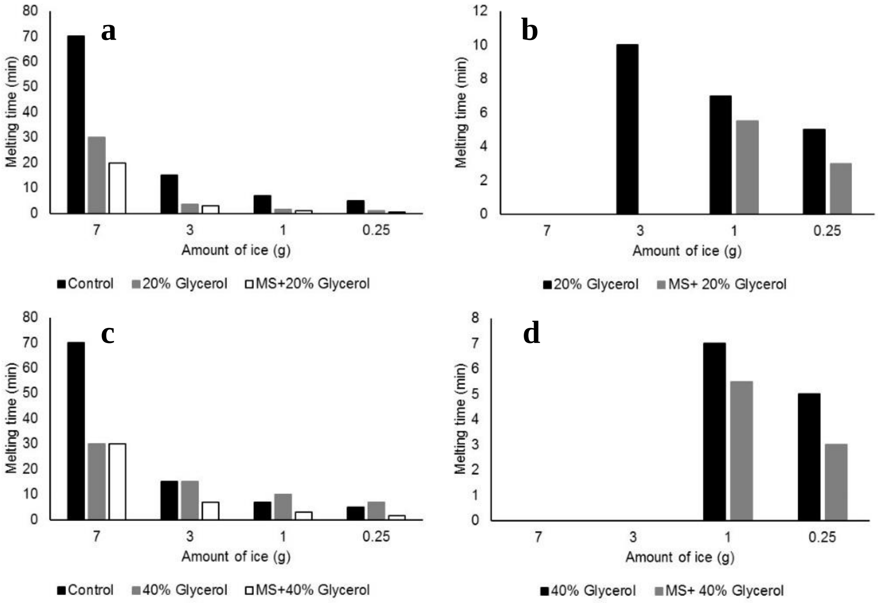

Figure 5. Comparison of MS particles with a) 20% Glycerol solution at +4°C b) 20% Glycerol solution at -16°C c) 40% Glycerol solution at +4°C d) 40% Glycerol solution at -16°C (MS particle: 0.24g; $KMnO_4$%:10)

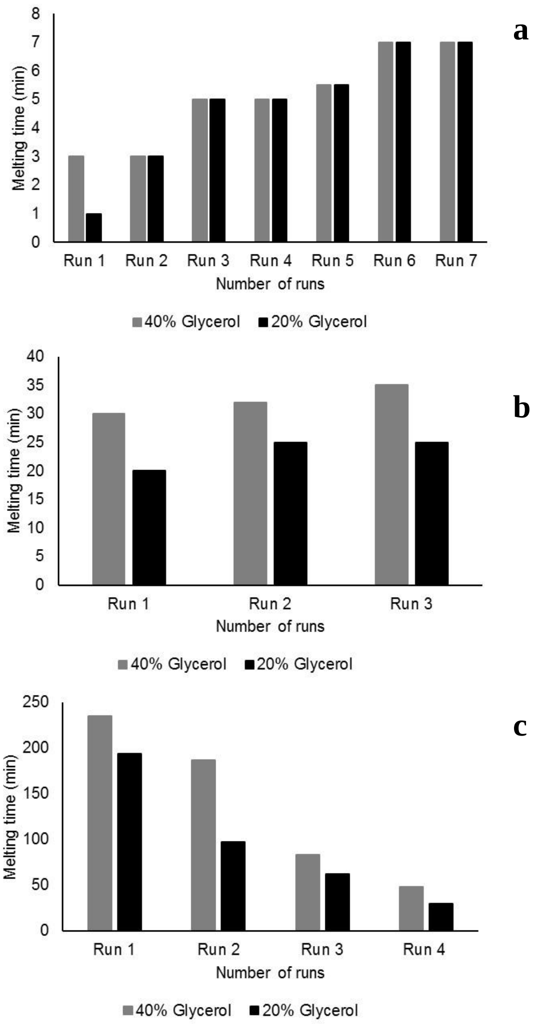

Figure 6. Effect of ice amount on repeated use of MS particles (0.24 g MS particle containing 10% $KMnO_4$) with a) 1 g ice b) 7 g ice and c) 15 g ice (Run indicates the number of repeated particle use)

Summaries

Combined utilization of starch modified with KMnO4 and glycerol was proposed for use as a de-icer alternative to glycerol and salt based de-icers. Results indicated an improvement in de-icing effect compared to sole glycerol utilization which was attributed to the exothermic reaction between glycerol and $KMnO_4$. Based on statistical analyses, the use of lowest amount of $KMnO_4$ with highest amount of MS particle was recommended to maintain environmental benign conditions. MS particles showed higher performance in elevated amounts of ice due to starch dissolution. Comparison of fresh and spent MS particles revealed higher performance values with lowest glycerol % in solution, in the presence of spent MS particles. This was the highlight of the study indicating the possibility of a decrease in glycerol utilization as de-icer.

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