

The Performance of Starch as a Natural Coagulant for Turbidity Removal from Wastewater in Stone Cutting Industry

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Background & Aims of the Study: In this study three types of starch such as wheat, corn and potato were used as natural coagulants for turbidity removal of wastewater in stone cutting industry using jar test and their performance was compared with that of alum.

Materials & Methods: This study is an analytical-applied. Natural wastewater from stone industry was used. The conventional jar test apparatus was utilized in all the coagulation-flocculation experiments. To evaluate the effect of gelatinized starch, the solution was prepared in both autoclaved and non-autoclaved forms. The effect of pH and coagulant doses were investigated in this study.

Results: It was found that with regard to the effect of control sample from autoclaved starches, potato starch with a pH of 6 had the highest removal rate with 4.78% and among non-autoclaved starches, wheat starch with a pH of 7 had the maximum turbidity removal rate with 9.53%.

Conclusions: The results showed that the non-autoclaved wheat starch has more efficiency in turbidity removal from wastewater in stone cutting industry than other starches.

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Background

The industry of stone cutting is one of the largest active industrial sectors and considered a major economic factor worldwide (1-2). During the cutting process, two types of solid and semi-liquid waste are produced (2-3). Stone slurry is a semi-liquid material consisting of particles following the use of water in order to facilitate cutting, cooling devices and prevent dust generated in this industry (2,4). Studies show that about 20 percent of the total weight

of the stone block is converted into slurry. The combination of slurry produced in the stone industry contains 96% water and is about 4% solid. Stone cutting industries are one of the industries with high consumption of water (1,5-6). Annual production of approximately 700,000 to 1,000,000 tons of slurry (7) and a prohibition of its discharge to public health systems have led to many problems in terms of disposal, environmental pollution and health risks (6,8-10). The discharge of these substances leads to the deposition of solid material in the downstream agricultural lands,

causing soil contamination and aquifers (1). This entry of wastewater into the environment causes environmental effects including an increase in the alkalinity of the soil, reducing the permeability of surface soils, loss of vegetation, soil erosion and topographic changes in the region (4,7).

It is necessary to prevent this type of wastewater from directly entering into the environment. To prevent environmental pollution, treatment of these types of wastewater is important (11-12). In the wastewater treatment in stone cutting industry, the physical-chemical methods- due to high levels of suspended solids- are more common (13). Coagulation and flocculation process is used as a comprehensive approach to water purification and industrial wastewater (13-14).

The coagulation and flocculation method is one of the methods which has come into prominence due to its simplicity of use, reliability, low power consumption and effective removal of turbidity, impurities and pathogenic bacteria (15-16). Alum, ferric chloride, ferric sulfate and synthetic organic polymers are the most commonly used coagulant materials (13,15,17,18). But the use of chemical coagulants is associated with many problems. The production of large volumes of sludge incurs heavy costs due to sludge disposal (14,19-20). Furthermore, epidemiological studies have reported a minimum 70% positive correlation between the presence of aluminum in drinking water and Alzheimer's disease (14,16-17,19).

Iron salts that require precise control of the process create sludge juicy (16). The relatively high purchasing costs, (15,21) inefficiency at low temperatures, (15,17) the ability to slow the destruction of the environment, (22) the long process of hydrolysis and the high dependence on pH due to coagulation are among the problems that arise from the use of chemical coagulants (23).

In order to prevent the secondary damage to human beings and the environment caused by the use of coagulants, there is a need to use alternative material (14-16). Nowadays, the use of natural coagulants has gained attention because of features such as low cost, non-corrosiveness and compatibility with the environment, biodegradability, availability, high reactivity, low sludge production and lack of dependence on pH (13,15-16,20,24).

Starch, one of the biodegradable polymers that can be used as a natural coagulant, is a natural resource found in abundance in the world (19,25-26). Due to the tear of starch granules and gelatinization affected by moisture and consequently an increase in viscosity, it has properties similar to coagulants. For this reason, it may be used in the process of coagulation-flocculation in the industries dealing with high turbidity (14).

In the study by Sook Yan Choy et al in the field of starch performance as a natural coagulant to remove turbidity, four types of starch, namely wheat, corn, potatoes and rice were used and the efficiency of turbidity removal in synthetic wastewater made with kaolin were studied in which autoclaved rice starch had the best performance by eliminating about 50% of the initial turbidity with a pH of 4, while taking into account the placebo effect (14). Another study by Chee Yang et al examined the use of rice starch to yield coagulation and flocculation in industrial wastewater, the starch performance regardless of placebo eliminates 84.1% of TSS in the pH of 3.5.

At present the supply of chemical coagulants for the industry of stone cutting wastewater treatment with high turbidity is a costly process (16). Starch is a natural, accessible and inexpensive source in the world (25). So, using it as a coagulant to remove turbidity in industrial wastewater such as stone cutting industry can have a very important role in economic terms. On the other hand, with regard

to the problems and risks associated with pollution from the industries mentioned above, the use of starch could somehow lead to management of industrial wastewater and reduce its organic load, which can prevent environmental degradation¹⁵).

Aims of the study:

As such, this study aimed to investigate the use of starch in the real wastewater treatment industry of stone cutting.

Materials & Methods

Materials

The present study utilized a pilot-scale experimental approach which was conducted using a jar test. Natural wastewater from stone industry was used for jar testing. Wastewater characteristics of the stone cutting industries are presented in Table 1. Three types of wheat, corn and potato starch (Merck) were used as natural coagulants. Distilled water was used to dilute hydrochloric acid (Merck) and to dissolve sodium hydroxide pellets (Merck) for the preparation of 1 M solutions to adjust pH samples.

Table 1) Wastewater characteristics

parameters	value
pH	8.25
Temperature(°C)	18
Turbidity (NTU)	6000±1500
TS(^{mg} / _L)	29160
TSS(^{mg} / _L)	23560
TDS(^{mg} / _L)	5600

Preparation of starch solution

Starch solutions with 3% concentration were prepared. To determine the effect of gelatinization of these solutions, both non-autoclaved and autoclaved starch solutions were prepared. To avoid the hydration of starch solution, these solutions were prepared fresh when needed during testing, and non-autoclaved starch solution with specified concentration were used directly in jar tests. As for preparing autoclaved starches, the solution

was sterilized for 15 minutes at the temperature of 121°C and pressure of 1.5 bar.

Since the residence time of wastewater from stone industry at settling ponds is two-hours, in this study the experiments were carried out using real wastewater having spent the settling time of 1.5 to 2 hours and Jar test was then performed with medium initial turbidity range of 168±5 NTU. All experiments were performed at the room temperature of 20 ± 2°C.

Coagulation-flocculation experiments

The conventional jar test apparatus (AQUALYTIC, JLT6, USA) was utilized in all the coagulation-flocculation experiments. In each test, 6 samples containing 500 ml of wastewater with specified turbidity were used and the starch solution as a coagulant with a specified concentration was added to it. Jar tests were set at 120 rpm for 1 minute for the rapid mixing, 40 rpm for 20 minutes for slow mixing stage and 30 minutes for settling time. After experiments, samples were taken at about 5 cm below liquid level using a glass dropper for analysis. The second phase of experiments was performed to determine the optimal pH and various amounts of pH ranging from 3 to 8 in the desired turbidity. To adjust the pH of samples, hydrochloric acid and sodium hydroxide 1 M were used via pH meter (METTLER TOLEDO, USA) at each stage of jar testing of control samples. A placebo (without the addition of any coagulants) was used under the same conditions of jar test with three replications of testing.

Measurement of coagulants

The overall changes in the starch structure of non-autoclaved as well as autoclaved starch solutions were observed using an inverted routine microscope (Eclipse TS 100, Nikon, USA). In order to determine the performance of flocs, the existing sludge sampling took place after Jar Test and analysis was performed after drying the samples using a microscope at a voltage of 10–15 kV.

Turbidity measurement methods

Turbidity was measured in terms of nephelometric units (NTU) using a calibrated turbidimeter (AQUALYTIC, USA). Initial and final turbidity samples were measured before and after the jar test. In this test, a sample of wastewater without adding any coagulant was used as the placebo and its final turbidity was measured after the final settling considered to be the final turbidity. The efficiency of coagulants at turbidity removal was calculated based on the following Eq. (1):

$$\text{Turbidity Reductions(\%)} = \frac{\text{Initial Turbidity Sample} - \text{Final Turbidity Sample}}{\text{Initial Turbidity Sample}} \times 100 \quad (1)$$

Results

In this study, a comparison was made between the chemical coagulant alum with starch as a natural coagulant. An understanding of the

optimal pH and doses of coagulant in chemical coagulation is very important, which can strongly influence the performance of the coagulant. For this reason, repeated experiments were performed in this study in order to determine the pH and optimal dose for each starch.

Characterization of coagulant

The starch powders and alum were characterized according to their bulk densities as well as crystallinity. The bulk densities obtained were in the increasing order of wheat, corn and potato starch (Fig.1).

In order to study the possibility of using starch as a natural coagulant to remove turbidity from industrial wastewater in stone cutting, the surface morphologies of these starches were also observed with the Scanning Electron Microscope (SEM) (Figure 1).

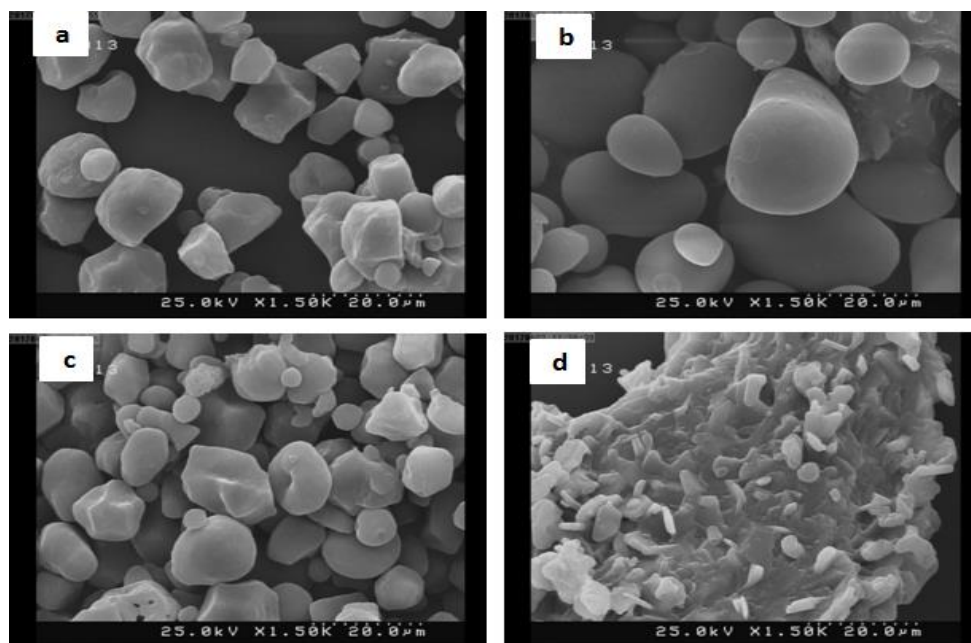


Figure 1) SEM images of conventional starches: (a) corn, (b) potato, (c) wheat and (d) Alum

The starch granules were distinguishable from their particle size and granule shape. Potato starch granules had the largest particle size while corn starch granules remained the

smallest. Besides, all the studied starches had smooth surfaces with the absence of pores.

Preparation of starch solutions

The starch solution was prepared and analyzed in autoclaved and non- autoclaved ways. Non-

autoclaved starch dissolve in water and starch particles are then deposited after a while. However, as can be observed in figure 2, the autoclaved starch granules absorb water after autoclaving and become swollen with an

increase in the viscosity due to rupture of the starch granules following water absorption.

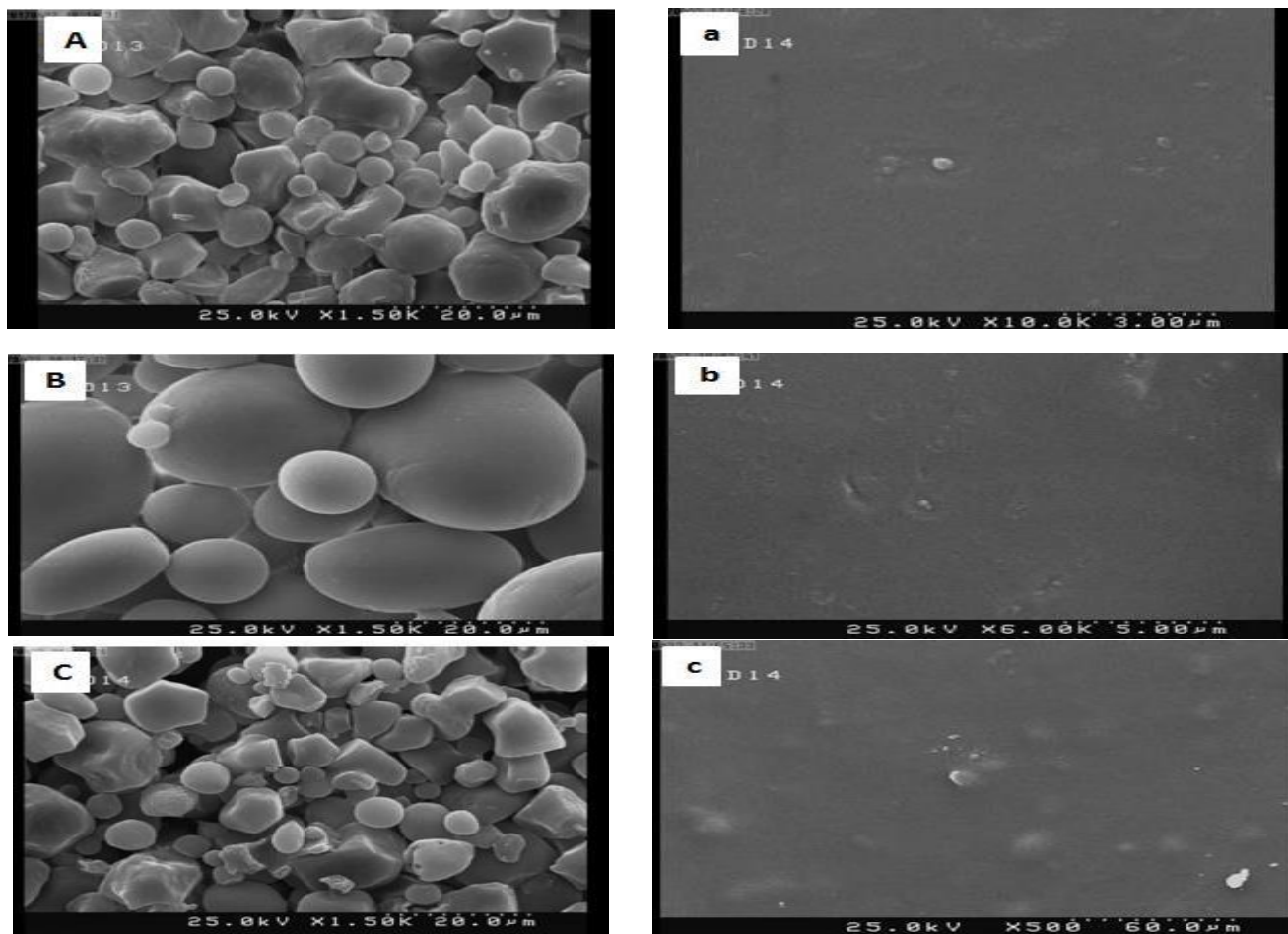


Figure 2) Structure of starch solutions when viewed under an microscope for (A, B, C) after and (a, b, c) before gelatinization of: (A, a) corn starch, (B, b) potato starch, (C, c) wheat starch

Use of starches as coagulants

In order to determine the effect of gelatinization in turbidity removal, starch solutions were prepared in two non-autoclaved and autoclaved forms and evaluated in the pH range of 3-8. The coagulant dose and the optimal pH for each starch were determined using Jar tests in the process of coagulation and flocculation. The results are shown in figures 3 and 4.

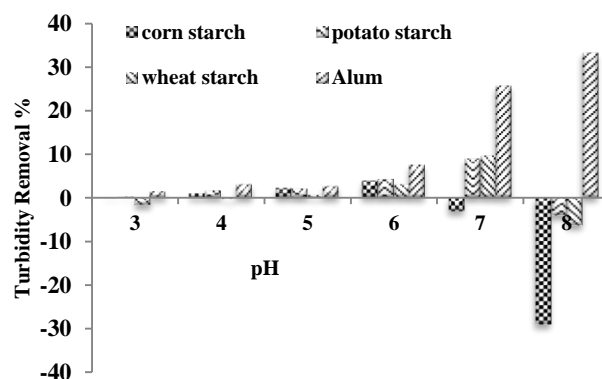


Figure 3) Turbidity removal achieved using various non-autoclaved starch solutions and Alum, at pH range of 3-8

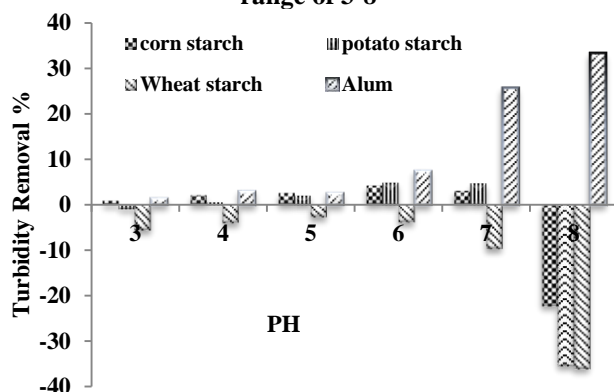


Figure 4) Turbidity removal achieved using various autoclaved starch solutions and Alum, at pH range of 3-8

Figure 3 shows the percentage of turbidity removal by non-autoclaved wheat, corn and potato starch in the wastewater of stone cutting industry. As has been shown in the chart, non-autoclaved corn starch with a pH of 4 to 6 had positive removal rate, with the highest removal of the starch occurring at the pH of 6. Non-autoclaved potato starch at different pH levels had positive removal rate except for the pH of 8 with the maximum turbidity removal from wastewater being 8.84% and occurring at pH of 7. Non-autoclaved wheat starch had positive removal at the pH range of 5-7 and had the highest removal of initial turbidity being 9.53% at the pH of 7.

Discussion

In this study three types of starch such as wheat, corn and potato were used as natural coagulants for turbidity removal of wastewater in stone cutting industry and their performance was compared with that of alum. The results showed that, turbidity increases at pH of 3, 4 and 8 with the reverse effect of using starch. Potato starch has negative removal only at pH of 8 and shows positive removal at various pH levels. The particles of this starch are bigger than other types of starch and perhaps this

bigger level causes the collision of these particles with the fine particles in the wastewater, leading to higher removal. (Figure 3) In the various examined starches, wheat starch had the most initial turbidity removal. In a similar study by Sook Yan Choy *et al* on the synthetic wastewater, non-autoclaved corn starch had negative removal in all pH ranges (14). While it shows a better performance in real wastewater in the stone cutting industry (current study). Non-autoclaved potato starch had an efficiency rate of turbidity removal rate close to that in real wastewater, having positive removal rate in all pH ranges except for pH of 8 with the highest turbidity removal occurring in synthetic wastewater. Wheat starch had negative turbidity removal rate in synthetic wastewater at all pH ranges except for pH of 4 with the removal percentage being about 11%, while this study showed a better performance with the positive removal rate at the pH range of 5-7.

Autoclaved wheat starch had negative removal in the pH range of 3-8. Non-autoclaved wheat starch showed a better performance in initial turbidity removal of wastewater compared with those by autoclaved types. Like the autoclaved and non-autoclaved potato starch had positive removal rate at pH range of 4-7. But, non-autoclaved potato starch had better performance. Autoclaved potato starch had the most removal rate being 4.78% at the pH of 6. Non-autoclaved wheat and potato starch showed better performance than the autoclaved ones in the initial turbidity, while this is not the case in non-autoclaved corn starch and the autoclaved type of this type of starch showed the highest removal rate. The autoclaved corn starch had a negative removal rate at the pH of 8, while it had a positive removal rate in other pH ranges, with a removal rate of 4.15%. This starch had the highest removal rate at the pH of 6. In a similar study, autoclaved corn starch had a positive removal rate in turbidity removal of synthetic wastewater at the pH of 9 and 10,

while showing a better performance at the pH of 10. However, in the present study except for pH of 8, positive removals have been observed at all pH levels. As mentioned earlier, autoclaved corn starch showed better performance at different pH levels in turbidity removal in industrial wastewater of stone cutting. In both studies, autoclaved potato starch had almost the same performance in real and synthetic wastewater, and positive removal has taken place in the pH range of 4-7, while autoclaved wheat starch shows opposite results and better efficiency in the case of turbidity removal from synthetic wastewater.

The results showed a positive percentage of initial turbidity removal using alum at different pH levels. The highest turbidity removal has happened at neutral and alkaline pH with the highest turbidity removal rate (33.25 %) occurring at pH of 8.

In a study by Ta Yeong Wu et al on the agro-industrial wastewater, the use of rice starch alone in room temperature enabled the removal of TSS up to 84.1% using the recommended values of dosage 2 g/L and initial pH 3(27). Higher TSS removal of 88.4% could still be achieved at lower dosage of rice starch (0.55 g/L) only when rice starch was used together with 0.2 g/L of alum during the treatment of POME. Also in another study by the same researcher, the response level method was based on the removal of TSS and COD; RSM showed that an addition of unmodified rice starch not only enhanced total suspended solids (TSS) and chemical oxygen demand (COD) removals; but it also significantly improved the process by reducing both the dosage of alum. The treatment enabled COD and TSS removals up to 49.23 and 86.65%, respectively under the optimum conditions of 0.28 g/L unmodified rice starch, 0.38 g/L alum and pH 4.45. The show of high removal in these two studies is

due to the neglect of the impact of the control sample, which we considered in our study of this effect (19,28).

Autoclaved corn starch showed a better performance in turbidity removal of industrial wastewater in stone cutting in comparison with the non-autoclaved one. This finding can be clearly observed in the related SEM images. Flocs produced from autoclaved corn starch have been formed better and bigger than its non-autoclaved ones (Figure 5). However, the non-autoclaved potato starch showed better efficiency than the autoclaved one in turbidity removal. According to Figure.3 flocs of non-autoclaved potato starch have a non-uniform and larger surface, which causes more collisions with particles caused by turbidity and hence a better performance. Autoclaved potato starch has formed smaller flocs and narrower surface compared to its non-autoclaved type. Therefore, it seems this has led to less impact with the ingredients causing turbidity and lower removal rate.

Wheat starch, demonstrates a similar performance like that of potato starch with the non-autoclaved one showing a better performance, which is clearly illustrated in Figure 3. Flocs of non-autoclaved wheat starch have formed larger levels, which makes it more likely to have a greater impact and lower negative removal in this research.

SEM images showed no significant changes in the structure of different types of autoclaved starch solutions in comparison with its powder and that only autoclaved solutions are crystallized by a little water absorption. Therefore, the gelatinizing properties of starch play a major part and crystallization may not have a direct impact on the performance of turbidity removal (14).

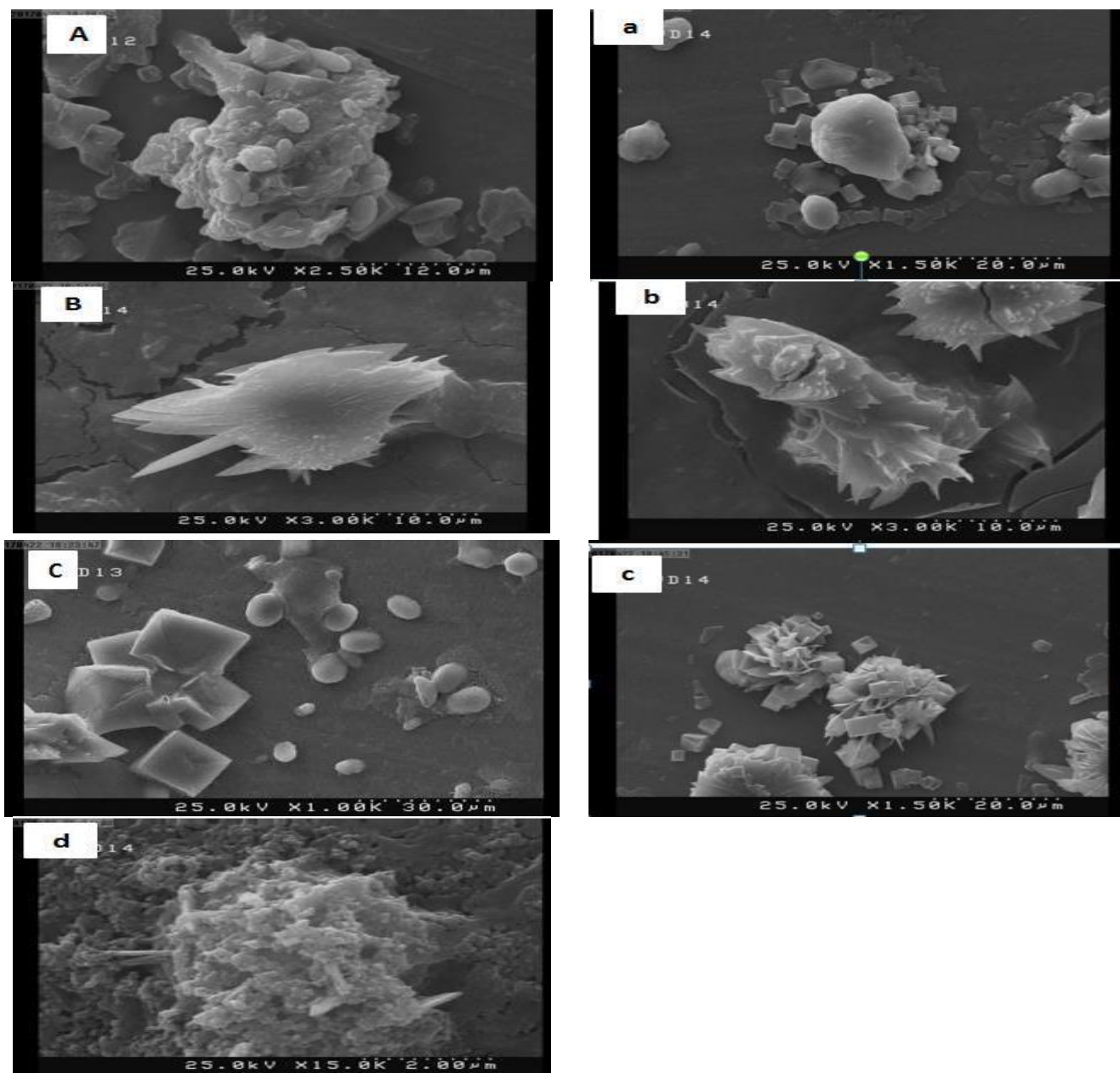


Figure 5) SEM images for starch solutions flocs generated from jar testing for (A, B, C) after and (a, b, c) before gelatinization of: (A, a) corn starch, (B, b) potato starch, (C, c) wheat starch and (d) Alum

Conclusion

The present study tried to shed light on the effect of the use of natural coagulant in both autoclaved and non-autoclaved types of starch in turbidity removal of wastewater from stone cutting industry. Autoclaved corn starch showed higher removal rate than its non-

autoclaved one, having the highest turbidity removal at pH of 6. In general, the comparison of different types of starch indicate that among the autoclaved starch, potato starch and from non-autoclaved starch, wheat starch have better performance. Furthermore, based on the comparison of alum with other types of starch, it was found that alum had positive removal

rates in all pH ranges and a rather similar performance to starch at low pH levels.

A good efficiency in turbidity removal can be achieved in wastewater from stone cutting industry without adding any type of coagulant simply by adjusting the pH level of wastewater.

Footnotes

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Conflict of Interest:

The authors declared no conflict of interest.

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