

REMOVAL OF BORON FROM INDUSTRIAL WASTEWATER BY CHITOSAN VIA CHEMICAL PRECIPITATION

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ABSTRACT

Chitosan is natural organic polyelectrolytes of high molecular weight and charge density; obtained from deacetylation of chitin. This study explored the potential and effectiveness of applying chitosan as a primary coagulant and flocculent for boron removal. A series of batch coagulation and flocculation processes with chitosan under different conditions, i.e. dosage, pH and temperature were conducted, in order to determine the optimum operating conditions for boron removal. The performance was accessed through total suspended solids (TSS), turbidity and boron concentration reductions. From the study, the optimum dosage for chitosan was recorded at 0.8 g/L with 94.2%, 91% and 79.7% for TSS, turbidity and boron, respectively. The optimum pH of 5 with the removal of TSS, turbidity and boron concentration were 97.8%, 93.4% and 87.5%, respectively. At the temperature of 60°C, the reduction of all the parameters (i.e. TSS, turbidity and boron concentration) was the highest compared to other temperature (i.e. 99%, 95.3% and 91% of TSS, turbidity and boron concentration reductions were achieved respectively).

Keywords: *Chitosan; boron; coagulation; flocculation; wastewater treatment*

1.0 INTRODUCTION

Boron is a soft, brown, nonmetallic element. It is extracted with some difficulty and in its reduced state appears as a substance of a deep olive colour, in a semi-metallic form, and in colourless quadratic crystals similar to the diamond in hardness and other properties. It usually does not occur alone, but is often found in the environment combined with other substances to form compounds called borates. Common borate compounds include boric acid, salts of borates, and boron oxide [1]. Boron and salts of borate have been found at hazardous waste sites. Boron alone does not dissolve in water nor does it evaporate easily, but it does stick to soil particles.

Water contamination by boron is one of the widespread environmental problems, since even a few parts per million present in irrigation water can cause stunting of plant growth. It even give a high impact to the microelectronic industries because the existence of trace amounts of boron in ultra pure water for cleaning and etching process can seriously influence the characteristics of semiconductor [2]. These facts show that the removal of ultra-trace, trace or large amount of boron is still a challenging problem. According to the Standard B of Malaysia Environmental

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Quality Regulation, the limitation of boron contents in waste water is only 4.0 mg/L. It will endanger to human being, animal and the whole environment as well if it's more than this limit. That is why continuous research has been done to find the best solution of removal boron from waste water [3].

There are several ways to reduce the contents of boron in wastewater such as separation by distillation, extraction, ion exchange, and separation by precipitation with organic and inorganic reagents [4]. First of all, most of the wastewater systems achieve treatment through a series of stages. It works out in a combination of biological, chemical and physical process. The primary stage often includes separating trash and large solid materials from the rest of the wastewater by screens or mechanically grinding them into finer materials. The remaining solids, oils, and greases are allowed to settle or separate from the rest of the stream in a septic tank, clarifier tank, or pond. The settled materials form a biologically active bottom layer of sludge.

The secondary stage of treatment uses a combination of biological and physical processes to reduce the amount of organic wastes. This can be achieved by filtering the wastewater through biologically active media, such as trickling filters; sand filters, or commonly uses an activated sludge process, where wastewater is exposed to both oxygen and the biologically active sludge, either through wind action or mechanical such as mixing and aeration. Tertiary treatment methods such as oxidation pond are sometimes required to reduce nutrients, toxic substances, or excessive amounts of dissolved materials in wastewater. Disinfection is often the final step after secondary or tertiary treatment and helps to kill most remaining viruses and bacteria. Yet, those traditional techniques as stated above were not efficient to reduce high content of boron in wastewater to reach the limitation of boron content in the Environmental Quality Regulation [5].

However, over the past few years, a growing effort has been devoted to application of chitosan on wastewater treatment. Chitosan is a natural polysaccharide with many useful features such as hydrophilicity, biocompatibility, biodegradability and the capability of adsorbing a number of metal ions because of its amino groups [6]. The ability of chitosan in adsorbing metal ions could be improved by several modifications on chitosan such as cross-linking, controlled N-acylation and N-alkylation with several functional groups.

Chitosan, known as poly[β -(1 \rightarrow 4)-2-amino-2-deoxy-D-glucopyranose], is a cellulose like biopolymer of high molecular weight obtained from deacetylation of chitin. Chitin, a linear chain polysaccharides, is the second most abundant organic material after cellulose, which is the major structural component of invertebrate exoskeleton, particularly in crustacean, mollusks and insects, as well as the principal fibrillar polymer in the cell wall of certain fungi[7]. Besides the reactive primary and secondary hydroxyl groups, chitosan's versatility as an adsorbent is a function of its highly reactive amino group at the C(2) position[8]. The protonation of the chitosan amino groups (NH_2) in solution makes the chitosan positively charged (exhibit as cationic polyelectrolytes) and thereby very attractive for flocculation and different kind of binding application, by allowing the molecule to bind to negatively charged surface via ionic or hydrogen bonding [9].

Chitosan offers a broad range of applications favour by unique properties of chitin and chitosan, such as biocompatibility, biodegradation, biological activity, non-toxicity, non-allergenic and ability for fiber and film formation. In water and wastewater treatment applications, chitosan have been used to synthesize membrane, used as an absorbent as well as primary coagulant or flocculent. Chitosan is

recognized as excellent metal ligands, forming complexes with many metal ions, thus enhance the removal of toxic metal from industrial wastewater. It has been shown to effectively remove metals such as boron [9], molybdenum, arsenic, gold, cadmium, vanadium, chromium, lead, cobalt, iron, manganese, silver, copper, nickel, mercury, and zinc from aqueous solutions [10]. In addition, it have been proved that chitosan could coagulate and flocculate a variety of suspensions or wastewaters including mash and lauter wastewater of brewery [11], fish-meal factories [12], mineral colloids [13], river silt[14], latex particles [15], microorganisms [16] and POME[17]. In this study, the effectiveness of chitosan as a coagulant for boron removal was assessed. A series of batch coagulation test was conducted to obtain the optimum dosage, pH and temperature by evaluating the parameters reduction such as boron concentration, turbidity and total suspended solids (TSS).

2.0 EXPERIMENTAL

2.1 Materials

The wastewater samples were taken from a metal manufacturing company operating in Senawang, Negeri Sembilan. The collected samples were then placed in a thermal resistant plastic container, sealed tight and labeled, before transported to the laboratory. For preservation, samples were refrigerated at about 4°C in order to prevent the wastewater from undergoing biodegradation due to microbial action. A portion of the samples was analyzed for its characteristic. Chitosan was purchased from Agros Chemical in the form of white fine powder.

2.2 Jar Test

A conventional jar test apparatus (Phipps and Bird stirrer, USA) was used in the experiments to coagulate boron wastewater with chitosan. It was carried out as a batch test, accommodating a series of six beakers together with six-spindle steel paddles. The wastewater samples were mix homogeneously before fractionated into the beakers containing 500mL of suspension each. Prior to the test, the samples were measured for boron concentration, turbidity and TSS for representing an initial concentration. After the desired amount of chitosan was added to the suspension, the beakers were agitated at various mixing time and speed, which consist of rapid mixing (250 rpm) for 15 minutes and slow mixing (30 rpm) for 30 minutes. After the agitation stopped, the suspension was allowed to settle undisturbed for 30 minutes. A sample was withdrawn using a pipette from the top inch of supernatant for boron concentration, turbidity and TSS measurements, representing the final concentration. The pH was controlled by adding either strong acid (5M HCl) or strong base (5M NaOH). All tests were performed at an ambient temperature in the range of 26-30°C.

2.3 Analytical analysis

Carminic acid method was chosen to determine the concentration of boron in wastewater. In this method, Spectrophotometer Hach Model DR2000 was used to measure the concentration of boron. Reagent Boro Version 3 with the presence of sulfuric acid was used in this experiment. Concentration of boron was determined by its reaction with carminic acid in the presence of sulfuric acid to produce reddish to bluish colour. The amount of colour was directly proportional to the boron concentration.

Turbidity was measured using HACH Ratio/XR Turbidimeter (HACH Company, USA). The measurement is based on the light-transmitting properties of

water. A gravimetric method was used to determine the TSS. With the aid of vacuum filtration apparatus, a retained solid on the filter was recorded after heating.

3.0 RESULTS AND DISCUSSION

3.1 Characteristic of wastewater before treatment

The characteristic of the wastewater was determined by measuring the boron concentration, turbidity, and suspended solid that contain in the wastewater. The purpose of the initial measurement was to ensure that a comparative result could be done before treatment and after treatment. The results of the characteristic of wastewater were shown at Table 1.

Table 1 Characteristic of raw wastewater

pH	boron concentration (mg/L)	Turbidity (NTU)	TSS (mg/L)
6.0	15.26	24.40	0.045

3.2 Effect of dosage on chitosan performance

According to Ahmad et al. (2005), the optimum dosage of chitosan to the boron removal was found to be in the range of between 0.4 g/L and 1 g/L. The effect of different chitosan dosage on the boron removal was analyzed. The experiments were conducted at seven different dosages of chitosan (i.e. 0.4 g/L, 0.5 g/L, 0.6 g/L, 0.7 g/L, 0.8 g/L, 0.9 g/L and 1 g/L) and were carried out at original pH and temperature of 30°C.

Chitosan, in this case, acts as a primary coagulant to destabilize, coagulate and further flocculate the suspension, and the results are presented in Table 2 and Figure 1. The results show that the increase of chitosan dosage lead to better coagulation performances (i.e. boron concentration, turbidity and TSS reductions) from 0.4 g/L to 0.8 g/L. However it can also be seen that from 0.8 g/L to 1 g/L the percentage of removals of those parameters decreased. The trends for all parameters are almost identical. Chitosan recorded the highest reduction of parameters for the applied dosage of 0.8 g/L, which were the reduction of 94.2%, 91% and 79.7% for TSS, turbidity and boron concentration, respectively.

Table 2 Effect of chitosan dosage on parameter reductions at pH 6 and 30°C

Chitosan dosage (g/L)	Percentage of boron reduction (%)	Percentage of turbidity reduction (%)	Percentage of TSS reduction (%)
0.4	27.5	61.9	82.9
0.5	37.7	66.4	84.2
0.6	58.4	70.5	86.2
0.7	65.9	80.7	92.9
0.8	79.7	91.0	94.2
0.9	64.1	84.8	91.1
1.0	34.5	69.3	83.1

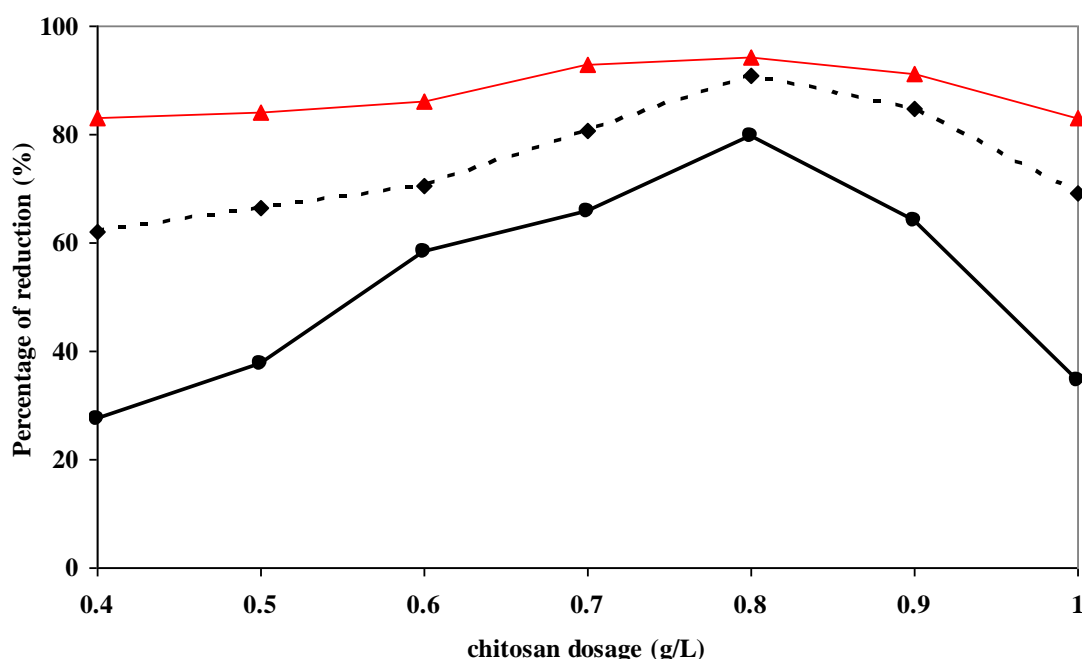


Figure 1 Effect of chitosan dosage on parameter reductions at pH 6.0 and temperature of 30°C. -▲- TSS, -◆- turbidity, -●- boron concentration

These results could be explained based on charge density. Chitosan has a high charge density compared to the other coagulants[17]. Moreover, polymer adsorption increased as the charge density of the polymer increased [18]. Therefore, this signifies the rapid destabilization of the particles; and can also be concluded that the amount of chitosan required to destabilize the particles is less for a coagulant of higher charge density, i.e. chitosan.

However, overdosing of chitosan beyond the optimal state causes the slightly decreased in removal efficiencies, as shown in Table 2 and illustrated in Figure 1. This could be due to reversal of surface charge as well as the restabilization of coagulated particles. Once the chitosan dosage exceeds the saturation of polymer bridging, surplus chitosan has a tendency to destroy the polymer bridging between particles, thereby exhibiting an increase in residual turbidity. Weber [19] indicated that polymer overdosing produces restabilized particles, due to unavailable site for the formation of bridges, resulting in the steric repulsion.

3.3 Effect of pH

The study of pH is essential to determine the optimum pH condition of the treatment system. The pH will not only affects the surface charge of chitosan, but also affects the stabilization of the suspension. The study was conducted by adjusting the pH from 4 to 9, temperature of 30°C, using the optimized dosage of each coagulant, i.e. 0.8 g/L of chitosan.

The parameter reductions for chitosan coagulation at different pH are shown in Table 3 and illustrated in Figure 2. By analyzing every curves in the figure for boron concentration, turbidity and TSS reductions; it can be stated that the pH has an influence on coagulation and flocculation processes using chitosan. The trends for all parameters are almost identical. The figure demonstrates that over 93% TSS reduction

can be achieved at pH 4, 5 and 6; of these the optimum is pH 5. At pH 5, the removal of TSS, turbidity and boron concentration were 97.8%, 93.4% and 87.5%, respectively. Nevertheless in pH > 6, the removal of TSS, turbidity and boron concentration decreased significantly. Therefore, chitosan demonstrates the best result of destabilization in slightly acidic condition, while portrays poorer efficiencies in strong acidic and alkaline condition.

Table 3 Effect of pH on parameter reductions at 0.8 g/L of chitosan and 30°C

pH	Percentage of boron reduction (%)	Percentage of turbidity reduction (%)	Percentage of TSS reduction (%)
4	75.7	80.0	93.3
5	87.5	93.4	97.8
6	79.7	91.0	94.2
7	48.2	61.0	80.2
8	41.0	55.5	64.4
9	34.5	48.8	53.3

This can be explained from the cationic nature of chitosan, which effected by the behavior of its functional amino group, and is strongly influenced by pH. Equation (1) describes the equilibrium reaction for amino group.



Reaction shift to the left as the concentration of H^+ ions increase. Ashmore and Hearn [15] pointed out that the equilibrium lies predominantly (99.97%) to the left at pH 4. It is known that strong acidic condition led to very strong cationic charge on chitosan. This situation is believed to create more possibility for particles restabilization due to reversal of surface charge. Besides that, at very low pH value, chitosan is very soluble and incapable in producing floc [20]. According to Schmuhl et al. [21], chitosan is unstable at pH 3. Therefore, it can be concluded that at pH below 5, the given concentration of chitosan causes the charge reversal of boron contaminated wastewater; and charge neutralization is the principal mechanism at low pH.

Although the differences between the plot at pH 4, 5 and 6 in Figure 2 are not very significant, but if based on the parameters' value, pH 5 provides the optimum TSS, turbidity and boron concentration reductions compared to other pH. Additionally, Domard et al. [22], pointed out that there are 90% of the functional group of NH_2 on chitosan surface has been protonated at pH 5, and gradually reduced to about 50% as pH increased to 7. Therefore, the positive charges on the chitosan surface will significantly decrease as solution pH increased, so the contribution by the charge neutralization of the chitosan to destabilize the particles becomes less important as pH increased. The properties of chitosan, including its cationic behavior and molecular weight, may be used both for charge neutralization (coagulating effect for anionic compounds) and for particle entrapment (flocculating effect) [23].

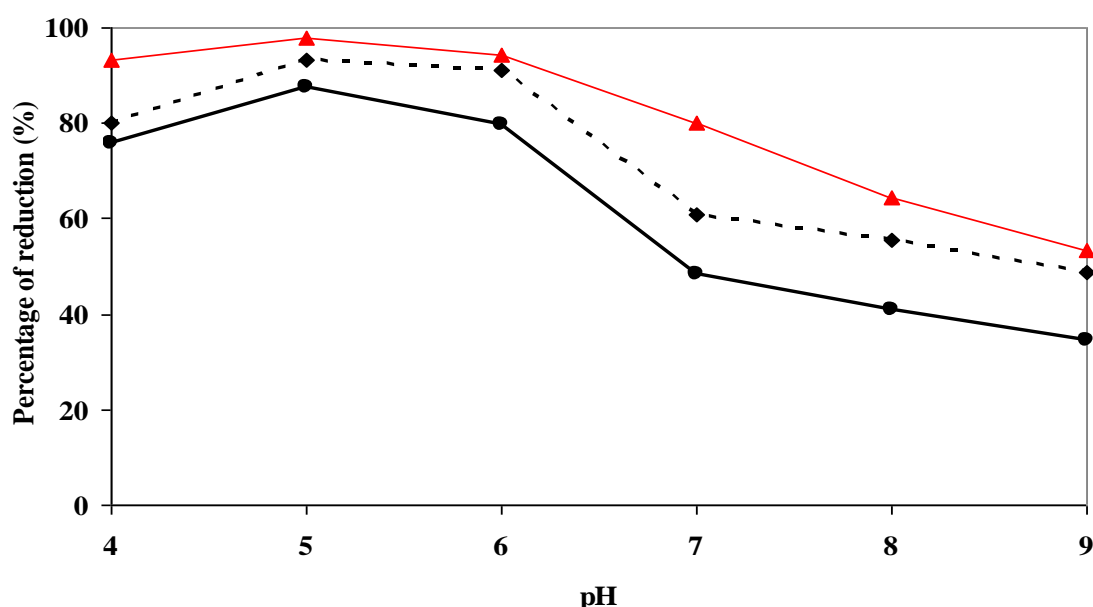


Figure 2 Effect of pH on parameter reductions at chitosan concentration of 0.8 g/L and temperature of 30°C. -▲- TSS, -◆- turbidity, -●- boron concentration

On the contrary, the efficiency of chitosan drops quite significantly at $\text{pH} > 7$, as shown in Figure 2. From the study of Huang and Chen [13], the isoelectric point of chitosan is about $\text{pH} 8.7$. Above this pH , chitosan loses its cationic nature, in other word positive charge on chitosan surface reduced significantly. Thus, bridging mechanism dominated the particles removal in this region. However, it is not strong enough to efficiently destabilize particles. Roussy et al.[23] also proved that chitosan at alkaline pH (i.e. $\text{pH} 9$) shows very low efficiency and required high concentration of chitosan to achieve the required treatment levels. This confirmed that protonation of chitosan amino group was required to achieve efficient coagulation of these organic suspensions. Beside the nature of chitosan, in alkaline condition, the surface of colloidal material has higher negative charge density due to the deprotonation of carboxylic or phenolic functional groups, so the particles become more stable [11].

3.4 Effect of temperature

The effect of temperature was investigated and the experiments were conducted at different temperature (50°C, 60°C, 70°C and 80°C). There had no literature that investigates the effect of temperature on the removal of metal ion or even residual oil. However there was a theory to support that temperature might give effect on the efficiency of boron removal [4].

Table 4 and Figure 3 show the effect of temperature on TSS, turbidity and boron concentration reductions at chitosan concentration of 0.8 g/L and $\text{pH} 5$. It can be seen that at temperature of 60°C, the reduction of all the parameters (i.e. TSS, turbidity and boron concentration) was the highest compared to other temperature and as the temperature increases, the percentage of TSS, turbidity and boron concentration reductions have reached plateau. For instance, 99%, 95.3% and 91% of TSS, turbidity

and boron concentration reductions were achieved respectively. According to Nemodruk and Karalova [4], at higher temperature boron compounds that contained in the wastewater could condensate better and removal of boron compound in the condensate had directly reduced the concentration of boron in the wastewater.

Table 4 Effect of temperature on parameter reductions at 0.8 g/L of chitosan and pH 5

Temperature (°C)	Percentage of boron reduction (%)	Percentage of turbidity reduction (%)	Percentage of TSS reduction (%)
30	87.5	93.4	97.8
50	88.7	94.3	98.0
60	91.0	95.3	99.0
70	90.0	94.8	99.0
80	90.0	94.7	99.0

The increased in amounts of boron adsorbed with temperature had confirmed the endothermic nature of the process [24]. Reaction rate constant was known to be dependent on temperature which the relationship could be explained in the Arrhenius equation to describe the temperature dependence. Since that it was an endothermic reaction, higher temperature had provided the chemical compound a sufficient kinetic energy to overcome the activation energy. Besides that, the larger pores form at the surface site enhanced the adsorption ability when heat was provided. This might also due to the fact that when low temperature, thermal energy was low. Therefore, the interaction between chitosan and boron compound was low because lack of thermal motion gave rise to form precipitation which mentioned in the study from Murray and Neville [25]. From that study, they also found that the precipitation process in cold water tends to be weaker than in room temperature.

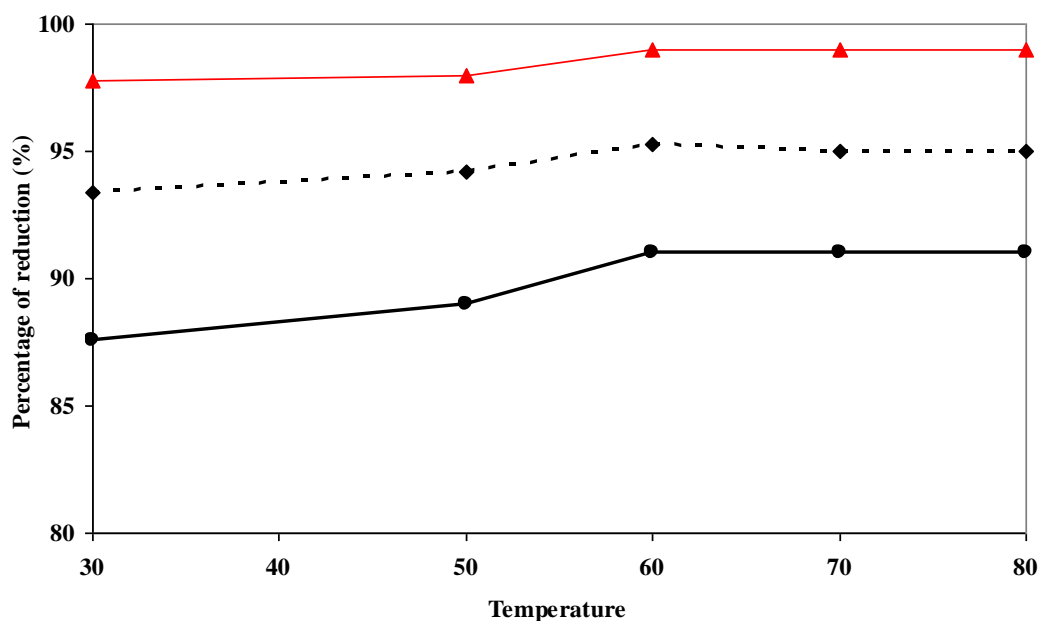


Figure 3 Effect of temperature on parameter reductions at chitosan concentration of 0.8 g/L and pH 5. --▲-- TSS, -◆- turbidity, -●- boron concentration

4.0 CONCLUSION

This study assessed the feasibility of chitosan for the removal of boron found in wastewater. It was found that the effectiveness of chitosan for boron removal was depending on the dosage, pH and temperature. Every changing of the parameter had affected the efficiency of boron removal, reduction of turbidity, and TSS removal. Chitosan promotes excellent parameter reductions (i.e. turbidity, TSS and boron concentration) which only required 0.8 g/L of dosage to give the best TSS, turbidity and boron concentration removals. Chitosan recorded the highest reduction of parameters for the applied dosage of 0.8 g/L, which were the reduction of 94.2%, 91% and 79.7% for TSS, turbidity and boron concentration, respectively. However, overdosing of chitosan beyond the optimal state causes the slightly decreased in removal efficiencies due to reversal of surface charge as well as the restabilization of coagulated particles.

At pH 5, the removal of TSS, turbidity and boron concentration were 97.8%, 93.4% and 87.5%, respectively. Chitosan demonstrated the best result of destabilization in slightly acidic condition (i.e. pH 5), while portrays poorer efficiencies in alkaline condition. This could be due to the positive charges on the chitosan surface will significantly decrease as solution pH increased, so the contribution by the charge neutralization of the chitosan to destabilize the particles becomes less important as pH increased. Additionally, at temperature of 60°C, the reduction of all the parameters (i.e. TSS, turbidity and boron concentration) was the highest compared to other temperature where 99%, 95.3% and 91% of TSS, turbidity and boron concentration reductions were achieved respectively. This could be due to the boron compounds that contained in the wastewater could condensate better at higher temperature and removal of boron compound in the condensate had directly reduced the concentration of boron in the wastewater. From all the best boron concentration removals for the effect of chitosan dosage (i.e. 0.8 g/L), pH (i.e. pH 5) and temperature (i.e. 60°C), the final boron concentration was below the Standard B limitation of Environmental Quality Act 1974 which is 4.0 mg/L.

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NOMENCLATURES

°C	-	Degree celcius
g/L	-	Concentration in gram per liter
mg/L	-	Concentration in miligram per liter
NTU	-	Nephelometric Turbidity Units
rpm	-	Rotation per minute
TSS	-	Total suspended solids

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