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Removal of silicon from pulping whitewater using integrated treatment of chemical precipitation and evaporation

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ABSTRACT

This article investigates and evaluates the technical applicability of integrated physico-chemical methods to treat thermo-mechanical pulping (TMP) whitewater collected from a local mill in Finland. Under optimized conditions, both chemical precipitation and evaporation were applied to remove silicon in the whitewater samples. The mechanism of silicon removal by the precipitant is also presented. Their treatment performances in removing silicon were statistically evaluated and compared to those of other reported studies. It is evident that both the treatments are applicable and effective to remove target pollutant from the samples. At the same SiO_2 concentration of 200 mg/L, 0.10 g/L of dose, pH 10.5 and 303 K, the integrated chemical precipitation using Fennofix type FF40 and evaporation could remove 96% of silicon. This finding is slightly higher than those of similar precipitation using CaO and electro-coagulation in other studies, which could accomplish 93% and 95% of silicon removal respectively at initial SiO_2 concentrations of 954 and 250 mg/L. Both chemical precipitation and evaporation could effectively treat a varying strength of TMP whitewater, as their treated effluents could meet the required silicon limit of less than 50 mg/L set by environmental legislation. Therefore, subsequent treatments are not required to complement the removal of silicon in the effluents prior to their discharge.

1. Introduction

From the very beginning, the excessive generation of wastewater effluents from pulp and paper industries worldwide has been identified as one of the environmental problems that need to be addressed to protect aquatic environment [1,2]. On average, each pulp and paper mill consumes a large amount of freshwater ranging from 10 to 60 m^3/tonne of pulp products [3,4]. However, it is difficult to recover 10% of their generated effluents for reuse [5,6].

Depending on pulping process, additive chemicals and wood materials, technology applied, and the amount of water consumed [7], wastewater effluents from pulp and paper mills are characterized by high strengths of chemical oxygen demand (COD) and a low biodegradability ratio of BOD_5/COD (Table 1) [8–12]. As ClO_2 is utilized in elemental chlorine-free (ECF) process for pulp bleaching [13], the mills generate effluents that contain toxic substances such as adsorbable organic halogen (AOX) and inorganic chlorine [14–16].

Resulting from thermo-mechanical pulping (TMP) of paper-making processing [17], the mills also produce TMP whitewater, which often causes corrosion problems in paper-making machines [18]. Depending on the type of raw materials and paper produced, paper-making technology and machines, and additive chemicals applied [19], the whitewater is characterized by a moderately high strength of COD and a low biodegradability ratio of BOD_5/COD (Table 1) [8–10]. The high concentration of COD in the whitewater is due to the lignin fraction (60%) that still remains after bleaching, while the remainder consists of carbohydrate (20%) and extractives (20%) [20].

In terms of environmental implications, the whitewater effluents contain not only wood components such as cellulose, fibres, and fillers, but also chemical additives involved in the paper-making processes such as soluble silicates ($3SiO_2{\cdot}Na_2O$), widely known as waterglass (Reaction (1)) [21]:

$$3SiO_{2(s)} + 2NaOH_{(aq)} \leftrightarrow Na_2O{\cdot}3SiO_{2(aq)} + H_2O_{(l)} \qquad (1)$$

Depending on pH, soluble silica exists in the form of $H_4SiO_4{}^0$, $H_3SiO_4{}^{-1}$, or $H_2SiO_4{}^{2-}$ in the aquatic environment with its concentrations ranging from 1 to 20 mg/L in surface water and from 7 to 45 mg/L in groundwater [22–24].

Due to its broad applications in industries in recent years, the global consumption of SiO_2 has rapidly increased to 9×10^9 m^3 annually [25]. Out of which, one-third is spent in the European Union every year [9]. In laundry industries, dissolved silicate is used for water softening, while in environmental business, it is

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employed as a corrosion inhibitor in piping [26]. In pulp and paper industries, apart from EDTA, the compound is applied as an auxiliary substance not only to brighten mechanical pulps, but also to stabilize H_2O_2 by inactivating metal ions such as Fe^{3+} and Mn^{2+}. Unless properly tackled, these metals may potentially catalyze the oxidant's decomposition during pulp whitening through the formation of manganese silicate [27–32]. With effluent concentrations ranging from 50 to 200 mg/L as SiO_2 [33], the presence of silica in the TMP whitewater is undesirable, as it reduces the heat-exchange efficiency of paper-making process, leading to an undesirable silica formation and deposition in the paper-making machines.

Since there is no feasible process other than cleaning and screening, the reclamation of whitewater effluents is economically important, since both the consumption of freshwater in the industries and the treatment cost of their effluents are very high. It is necessary to recover valuable materials in the effluents through recirculation, as this minimizes environmental stress due to the release of toxic compounds into the environment [34]. If SiO_2 concentration in the whitewater exceeds 118 mg/L – which is its solubility at pH ranging from 6 to 8 [35,36], – the recirculation of silica accumulates organic matter in the paper-making machines, thus resulting in the clogging of the equipment and/or siliceous scaling deposit in pipes.

This inorganic deposit contains not only SiO_2, but also a complex mixture of all the substances involved in the paper-making process such as filler, fibres, resins and sizing agents [33]. It is difficult to remove SiO_2 deposit in the machines once it is formed. Unless properly treated, the deposit of such contaminants in the pipes can be detrimental to the efficiency of a pulp and paper mill, as it reduces the quality and operating efficiencies of the products. This problem not only results in the quality defects in the finished paper products, but also shortens equipment's life and impairs the system operations in paper mills [35].

Apart from these technical aspects, the public concern about SiO_2 stems from the fact that the discharge of the whitepaper effluents into the aquatic environment adversely affects aquatic organisms in the long-term. This could be due to the fact that the main component of soluble silicates is silicon that can be transformed into a biologically active orthosilicic acid monomer either as H_4SiO_4 or $Si(OH)_4$ (Reaction (2)), depending on its pH [37].

$$SiO_{2(s)} + 2H_2O_{(aq)} \leftrightarrow H_4SiO_{4(aq)} \leftrightarrow Si(OH)_{4(aq)} \qquad (2)$$

Unless properly treated, the presence of dissolved silica in whitewater results in a number of environmental problems such as high concentrations of organic matter in the aquatic environment that leads to oxygen depletion in receiving rivers and the generation of toxic H_2S. Consequently, the silicate not only changes population structure [38], but also accumulates phytoplankton biomass in receiving rivers by decreasing the N/Si and P/Si ratios. This leads to the uncontrolled growth of diatoms over the other groups of algae that may ruin terrestrial systems in the long-term [39]. For these reasons, treatment of pulping whitewater is required.

To promote "zero liquid discharge", recently technologies that avoid the consumption of toxic chemicals have been employed [40]. Because of no energy consumption, an integrated anaerobic digestion and activated sludge have been applied to reduce COD concentrations in TMP whitewater [41]. In spite of its effective removal for COD, the high content of H_2S in the effluents hinders this combined treatment from being widely used [42].

Advanced oxidation processes (AOPs) using ozonation [43], electro-oxidation [44], ultrasonication [45], and Fenton's oxidation [46] were also employed to treat contaminated wastewater. However, these technologies are not cost-effective when the concentration of dissolved silicon in whitewater is low, while the volume of the wastewater is large [47,48].

Table 1
Characteristics of wastewater effluents from pulp and mill industries.

Parameter	Type of wastewater		Reference
	Bleaching effluents	Whitewater effluents	
pH	10	4.2	[3,4,8–10]
BOD_5 (mg/L)	568–5000	770–1800	
COD (mg/L)	1124–13000	1900–3500	
BOD_5/COD	0.04–0.38	0.02–0.07	
AOX (mg/L)	12.5	NA	
SS (mg/L)	383–810	17–40	
Nitrogen (mg/L)	–	3–13	
Phosphorus (mg/L)	–	0.5–1.8	

Remarks: NA: not available; AOX: adsorptive organic halogen; BOD: Biochemical oxygen demand; COD: Chemical oxygen demand; SS: suspended solids.

Table 2
Effluent limits of pulp and paper mills' wastewater.

Parameter	Discharge limits (kg/ADt)			Reference
	Finland	US EPA	Canada	
BOD_5	6.8–34	2.41	5.5–30	[3]
COD	90	NA	NA	[4]
AOX	1.4	0.27	1.4–1.5	[8]
SS	5–15	3.86	1	[10]
SiO_2 (mg/L)	50	50	50	[8,10,37]

Remarks: NA: not available. ADt: air dried metric tonne of produced pulp; AOX: adsorptive organic halogen; BOD: Biochemical oxygen demand; COD: Chemical oxygen demand; SS: suspended solids.

Due to the stringent effluent limit set by environmental legislation (Table 2), there is a growing need to explore other technologies that not only offer high removal performance, but also generate treated effluents that can meet the requirement of effluent limit. Due to its capability of treating a large volume of whitewater effluents containing high concentrations of silicon, chemical precipitation may be employed. After pH adjustment to basic conditions (pH 10–11), target compounds may be converted into an insoluble solid phase. This method is economically attractive, as it may give a high removal of target compounds at low cost.

Table 3
Characteristics of whitewater samples.

Parameter (unit)	Primary clarification		
	Before	After	Difference (%)
pH	7.5	8.5	13.33
Temperature (°C)	80	79	1.25
BOD_5 (mg/L)	1300	1275	1.92
COD (mg/L)	2890	2850	1.38
BOD_5/COD	0.45	0.48	6.66
SS (mg/L)	140	130	7.14
TOC (mg/L)	2500	2549	0.04
Fatty acids (mg/L)	29	25	13.79
Resin acids (mg/L)	25	24	4.00
Lignans (mg/L)	2	1.75	12.50
Sitosterols (mg/L)	4	3.80	5.00
Sterylesters (mg/L)	49	45	8.16
Triglyserides (mg/L)	106	103	2.83
Turbidity (NTU)	1700	1400	17.64
Conductivity (mS/cm)	5.5	5.3	3.64
Dissolved Si (mg/L)	60	60	0
Total SiO_2 (mg/L)	200	200	0
Ca^{2+} (mg/L)	43	42	1.19
Al^{3+} (mg/L)	2.1	2.0	4.76
Mg^{2+} (mg/L)	9.3	8.9	4.30
Mn^{2+} (mg/L)	1.5	1.5	0
Fe^{2+} (mg/L)	1.4	1.3	7.14
Na^{+} (mg/L)	1600	1595	0.62
$SO_4{}^{2-}$(mg/L)	240	238	0.83

AOX: adsorptive organic halogen; BOD: Biochemical oxygen demand; COD: Chemical oxygen demand; SS: suspended solids.

Since the TMP whitewater also contains dissolved solids such as Fe^{2+} and Mn^{2+} (Table 3), evaporation may be effective for concentrating and completing their removal. During evaporation, components with vapour pressure higher than that of wastewater transfer to the condensate, while the most non-volatile organic/inorganic components of the solutions are transferred to the concentrate [49]. In this regard, the silicon in whitewater could be concentrated and then subsequently separated by evaporation.

For this reason, integrating both the physico-chemical treatments may be technically applicable, as precipitation and evaporation may synergistically enhance silicon removal from the whitewater. Precipitation is not only tolerant to toxic pollutants and varying temperatures, but also able to accommodate varying loads and flows of the effluents, while evaporation may recover valuable materials in the effluents to minimize the loss of raw materials from the paper-making machines.

The laboratory study reported in this article investigates and critically evaluates the effectiveness of integrated physico-chemical methods in treating TMP whitewater collected from a local ground wood mill. Under optimized conditions in batch modes, the combined chemical precipitation and/or evaporation were applied to remove silicon from whitewater effluents. Their treatment performances in removing the target compound from the samples were statistically evaluated and compared to those of other studies reported in the literature.

2. Materials and methods

2.1. Materials

The samples of TMP whitewater effluents were collected from a local ground wood mill that employs elemental chlorine-free (ECF) process. As an integrated pulp and paper mill, the industry consumes about 0.25 m^3 of Norway spruce pulping wood (*Picea abies*) as the main raw material and 45 m^3 of freshwater to produce 1 tonne of pulp products. Annually the mill produces 170,000 tonnes and 120,000 tonnes of hardwood and softwood pulp respectively. With an overall design capacity of 50,000 m^3 of wastewater per day, its treatment plant treats about 45,000 m^3 of effluents daily. Since its first operations, the plant has employed activated sludge to treat whitewater after applying preliminary sedimentation or flotation to remove suspended solids and coarse particles.

After their collection from the same sampling points—where the primary effluents were well mixed [50], the samples were immediately transferred into 20 L polyethylene carboys that were filled to capacity and capped tightly. To minimize any changes that might occur in their physico-chemical properties prior to the experiments, the freshly collected samples were stored in a refrigerated storage chamber at 4 °C. After centrifugation and filtration using 0.45 μm polypropylene membrane (VWR Finland), the effluent samples were immediately characterized according to the Standard Methods [51] for the following parameters: pH, COD, BOD_5 (biochemical oxygen demand), TOC (total organic carbon), suspended solid (SS), dissolved SiO_2, and heavy metals. After their characterization, the samples were subsequently used for a series of batch experiments under identical conditions.

Prior to treatments, pH of the raw samples was measured using a pH meter model VWR pH 100 (Finland). Adjustment of the pH was carried out using 0.1 M NaOH and/or 0.1 M HCl. The concentrations of COD were analyzed by a UV/VIS spectrophotometer model Lange DR 2800 (Germany) based on the closed reflux colorimetric method (Standard Methods 5520D), while total organic carbon (TOC) and the conductivity of the samples were measured using a TOC analyzer type Shimadzu 5000 A (USA) and a conductivitimeter type VWR EC 300 (Finland) respectively. Sulphate ions were analyzed using a selective electrode type Orion 96-17 (USA).

Table 4
Physical properties of Fennofix samples.

Properties	
Appearances	Colorless
Viscosity (cps)	50–150
pH	3–5
Solid contents (%)	48–52
Density (g/cm^3)	1.21

Unless otherwise stated, all the chemicals including the precipitants' samples were of analytical grade supplied by Kemira Chemicals Oy (Finland) and used without further purification. Ultrapure water with resistivity higher than 18.2 MΩ cm was employed throughout the experiments to prepare all the working solutions and reagents.

2.2. Methods

2.2.1. Chemical precipitation

To investigate its effectiveness for silicon removal, chemical precipitation of the collected samples was undertaken in 100 mL reactors. The dose of the precipitants was varied from 0.02 to 0.12 g/L, while the solution pH was varied 6.5 from to 11.5. Subsequent experiments were carried out only with optimized parameters. Prior to experiments, the reactors were tightly covered with Teflon sheets to prevent possible contamination by any foreign particles. Predetermined concentrations of precipitant were added into the samples containing SiO_2, while keeping pH constant.

To homogenize them, the samples were mechanically stirred in a temperature-controlled water bath at a higher agitation speed of 400 rpm for 1 min, followed by a low stirring at 100 rpm for 9 min to promote flocs formation through agglomeration. Control studies were also conducted in the form of corresponding tests that did not contain target compound. After settling for 30 min, the samples were withdrawn from the reactor and their pH was measured. After separating the samples from the flocs by centrifugation at 500 × g for 15 min, their supernatant was collected and analyzed for silicon and zeta potential, while the flocs were discharged [56].

To optimize silicon removal, the pH of the samples was varied from 5.5 to 11, while applying the optimum dose as constant. The precipitants applied in this study included Fennofix (FF). This quaternary ammonium cationic polymer, widely known as quats, is positively charged polyatomic ions of the structure NR_4^+ with R being the alkyl groups. This can be used as a cationic monomer to form copolymer and homopolymer by various polymerization reactions. Its properties are presented in Table 4. These polymers have various similar types such as FF40, FF50, FF210, FF220, FF230 and FF240, but different level of cationic charge density to a certain extent. Their cationic charge densities decrease with an increase in the product numbers. For example, FF40 and FF 50 have higher charge densities than their corresponding products in 200-series.

2.2.2. Determination of zeta potential

As the whitewater samples contain a variety of colloidal matter, refractory compounds, and other dissolved organics, it is necessary to determine the zeta potential of its complex mixture before and after precipitation treatment. In this study, their zeta potential (ζ) determination was undertaken at ambient temperature in 100 mL glass beakers using a Malvern zetasizer instrument type Nano-ZS (Malvern, Britain). This equipment poses a laser Doppler velocimetry to analyze the electrophoretic mobility of the samples. After completing a series of measurement for each collected sample, the zeta potential was calculated using the following formula (Eq. (3)):

$$\mu_e = \frac{\varepsilon_r \varepsilon_o \zeta}{\eta_1} \tag{3}$$

where ε_r and ε_o represent the dielectric constants of the medium and free space, respectively, while μ_e and η_1 are the electrophoretic mobility and liquid viscosity, respectively [53].

2.2.3. *Integrated chemical precipitation and evaporation*

With an evaporation area of 1 m^2 and its capacity of 3 L/h, an apparatus model GEA Niro (Columbia, US) consisted of a 1 L pyrex flask in a thermostatic bath, a thermometer, a cooler, 100 mL graduated cylinder of condensate collection, a pressure gauge, and a rotative vacuum pump. At an optimum pH 10.5, evaporation of treated effluents, resulting from precipitation pre-treatment, was subsequently carried out in a vacuum evaporation (rotovapor) device using a hotplate as the heat source. At varying temperatures from 313 to 373 K, the vapour was compressed at 50,000 Pa of pressure. The vapour flew through to the outside of the reactor, where its heat passed through to the cooler inside. As the vapour transferred its heat, it condensed as distillate after 2 h. Afterward, predetermined volume of treated effluents, resulting from the earlier precipitation, was added to reconstitute the initial volume of 100 mL. At designated time, the condensates were collected and analyzed for silicon [54]. The operations were repeatedly conducted to attain a steady state in the condensed samples. Resulting from this evaporation, the solids containing silicon were collected in the concentrate and then disposed of, while the water might be reused.

2.2.4. *Chemical analyses of total silicon*

Changes in the concentration of total silicon (including soluble and colloidal SiO_2) after individual and/or integrated treatment were determined according to the Standard Methods (4500-Si) [51]. The optical density of the yellow complex of molybdosilicic acid, resulting from the reactions between ammonium molibdate, filtered samples, and oxalic acid, was colorimetrically measured using a UV spectrophotometer at a wavelength (λ) of 380 nm, while the blue-colored silico-molybdic, resulting from the reduction of the yellow-colored molybdosilicic acid by 1-amino-2-naphtol-4-sulfonic acid, was measured at 810 nm of wavelength. The blue color of the complex was more intense than its corresponding yellow one. The minimum detectable concentration using this method is approximately 1 mg/L as dissolved SiO_2. Tartaric acid was also applied to remove interferences from phosphorus by destroying phosphomolybdate. The % removal (E) of silicon after treatment is defined as:

$$E(\%) = \left[\frac{C_o - C_e}{C_o}\right] \times 100 \tag{4}$$

where C_o and C_e are the initial and equilibrium concentrations of silicon in the whitewater samples (mg/L) respectively.

2.3. *Statistical analysis*

All the experiments were conducted in triplicate under identical conditions and the results were presented as the average value of three data sets. In most cases, the relative standard deviation was less than 1%. In a few cases, where the relative errors of silicon removed by either of the individual treatment method exceeded 5%, the obtained data were disregarded and an identical fourth run would be undertaken until the relative error fell within this criterion. To determine the margin of error, a confidence interval (CI) of 95% was calculated for each set of the samples and the obtained data were analyzed using *t*-test and/or ANOVA test. Differences were considered statistically significant when $p \leq 0.05$ for the analysis of variance (ANOVA) or *t*-tests.

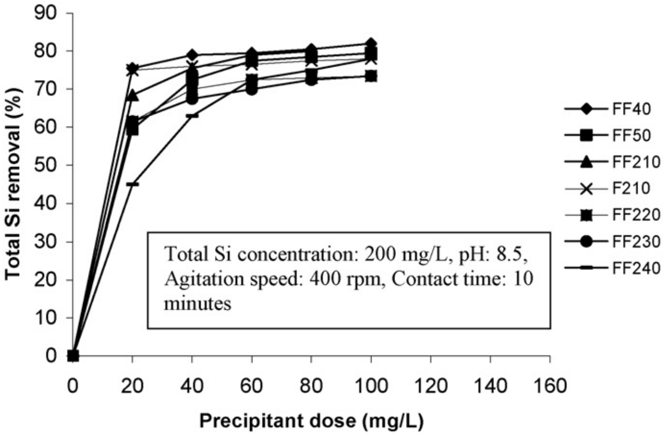

Fig. 1. Effects of precipitant dose on silicon removal.

3. Results and discussion

3.1. *Characteristics of whitewater samples*

In the local mill, sedimentation or flotation was involved in primary clarifier to remove suspended solid from the effluents. Their physico-chemical characteristics before and after primary clarification are presented in Table 3.

It was observed that the biodegradability (BOD_5/COD) ratio of the whitewater samples slightly increased from 0.45 to 0.48 after primary clarifications. Most of the organic materials in the samples contained refractory substances and slowly biodegradable materials. This indicates that the samples are better treated with physico-chemical treatments than with biological process.

In addition, the TMP whitewater effluents also contain inorganic substances including Ca^{2+}, Mg^{2+}, and Al^{3+} (Table 3), as indicated by their conductivity values [55,56]. The conductivity of the whitewater samples improved with an increasing dose of the Fennofix precipitant due their improving cationic charge. Due to the presence of the heavy metals [57–59], chemical precipitation was selected to preliminarily treat the whitewater effluents.

3.2. *Effects of precipitant's dose on total Si removal*

The removal of total silicon in the whitewater samples corresponds to the amount of a precipitant present in a reactor. In this regard, the amount of precipitant required for an effective precipitation depends on the characteristics of wastewater, degree of clarification, and BOD reduction required [60]. For this reason, it is necessary to determine the optimum dose of precipitant to maximize silicon removal from the samples. In this study, the dose of Fennofix precipitants was varied from 0.02 to 0.12 g/L with an increment of 0.02 g/L and applied to the samples that contained 200 mg/L of SiO_2, while pH was kept at pH 8.5, the initial pH of whitewater samples after primary clarification.

Fig. 1 demonstrates that the removal of silicon by various organic polymers acting as a precipitant improved with their increasing doses. This stemmed from the fact that with an increasing dose, more silicon could be precipitated in alkaline environment. As seen in Fig. 1, about 82% of silicon removal was achieved by the Fennofix precipitant type FF40 at 0.10 g/L, while at the same dose and initial concentration of 200 mg/L, other Fennofix precipitants (FF 220 and FF230) could only remove 73% of total silicon. Beyond 0.10 g/L of FF40, no significant increase in the silicon

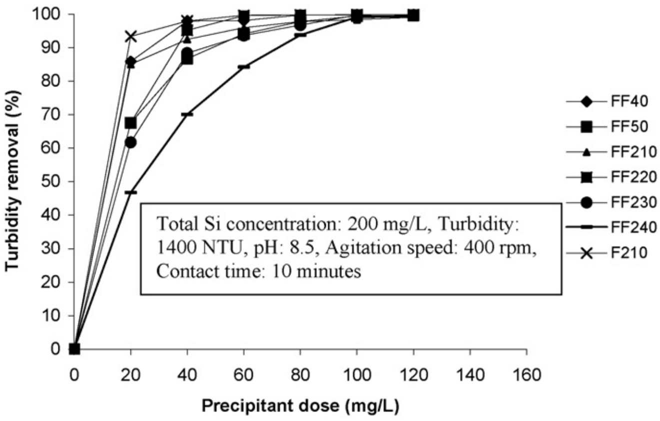

Fig. 2. Dose dependence on turbidity removal.

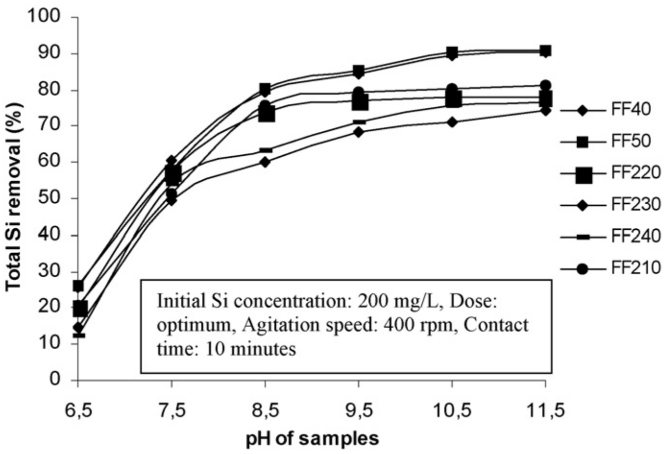

Fig. 3. Effects of pH on silicon removal.

removal was observed after 30 min of reaction. Therefore, 0.10 g/L was selected as the optimum dose of FF40 for Si removal.

Compared to other precipitant such as lime applied in other reported studies [5,36], the FF40 precipitant employed in this study required a significantly lower optimum dose to attain a comparable level of silicon removal. Another advantage is that the separation of precipitates from the treated whitewater would be difficult if lime were applied as the precipitant, considering that the precipitate of other amphoteric metals such as Al(III) would dissolve if their pH changed beyond the optimal range.

At 0.1 g/L of dose, the silicon concentration in the treated effluents was reduced to 36 mg/L, which was lower than 50 mg/L, the acceptable effluent limit set by environmental legislation [10] (Table 2). At the same operating conditions and initial turbidity of 1400 NTU, an almost complete removal of turbidity was accomplished by FF40 (Fig. 2). This finding indicates the effectiveness of this precipitant for removing both silicon and turbidity in the samples. This result suggests that subsequent treatments such as activated sludge are not required to complement silicon removal in the whitewater effluents prior to their discharge.

3.3. *Effects of pH on total Si removal*

The extent of chemical precipitation for silicon removal is affected not only by the chemistry of the target compound, hydration and dissolution of the precipitant, but also by pH, which enhances the flocculation properties of target compound [52]. For this reason, pH dependence of silicon removal was studied by varying its value from 6.5 to 11.5.

Fig. 3 presents the effects of pH on the silicon removal by precipitation. It is noticed that the precipitation of silicon by all types of Fennofix was dependent on the initial pH of the samples. The maximum removal of Si occurred at pH ranging from 8.5 to 11.5 ($p > 0.05$; Anova test). At pH higher than 7.5, the polymerization rate of colloid silica that dissolves H_2SiO_3 monomer proceeded rapidly [36]. At pH 10.5, about 90% of total Si removal was achieved by Fennofix type FF40, while at the same initial concentration of 200 mg/L, FF230 and FF 240 could remove 75% and 77% of Si respectively.

To understand the mechanism of silica removal by the precipitant, it is necessary to understand the speciation of dissolved silicate in aqueous solutions (Reactions (5)–(8)).

$$SiO_{2(s)} + 2H_2O \leftrightarrow H_4SiO^0_{4(s)} \quad K_{SiO_2} = [H_4SiO^0_4] \tag{5}$$

$$H_4SiO^0_{4(s)} + H_2O_{(l)} \leftrightarrow H_3SiO^{-1}_{4(aq)} + H_3O^+_{(aq)} \quad k_1 = \frac{[H_3SiO_4^{-1}][H^+]}{[H_4SiO^0_4]} \tag{6}$$

$$H_4SiO^0_{4(s)} \leftrightarrow H_2SiO^{2-}_{4(aq)} + 2H^+_{(aq)} \quad k_2 = \frac{[H_2SiO^{2-}_4][H^+]^2}{[H_4SiO^0_4]} \tag{7}$$

$$[Si_{total \quad dissolved}] = [H_4SiO_4{}^0] + [H_3SiO_4{}^{-1}] + [H_2SiO_4{}^{-2}] \tag{8}$$

where k and K_{SiO_2} represent the equilibrium constants of each species and SiO_2 respectively [24]. At pH ranging from 2.5 to 7.5, silica exists as SiH_4 species, which lacks ionic charge and is unstable in aqueous solutions [24]. According to the Pourboix diagram, the SiH_4 area of stability is below the lower limit of water stability in a potential-pH diagram. At pH higher than 7.5, silicate in whitewater is present in the form of orthosilicic acid $[H_2SiO_4{}^{2-}]$ (Reaction (9)) [23]. In basic conditions, the solubility of dissolved silica increases due to the formation of $H_2SiO_4{}^{2-}$ ions [35].

$$2Si + 2OH^-{}_{(aq)} + 2H_2O_{(l)} \leftrightarrow H_2SiO_4{}^{2-}{}_{(aq)} + SiH_{4(g)} \tag{9}$$

At pH higher than 7.5, the OH^- concentrations gradually increased and facilitated the ionization of silicic acid ($H_4SiO_4{}^0$) into $H_3SiO_4{}^{-1}$, its stable anion (Reaction (10)):

$$H_4SiO_4{}^0 + OH^-{}_{(aq)} \rightarrow H_3SiO_4{}^{-1}{}_{(aq)} + H_2O_{(l)} \qquad pKa = 9.84 \tag{10}$$

In an alkaline environment, both $H_3SiO_4{}^{-1}$ and $H_2SiO_4{}^{-2}$ are the most predominant forms of dissolved silica, while at neutral pH ranges, silica is present as $H_4SiO_4{}^0$ [24].

In this regard, optimizing the operating pH at alkaline conditions, while applying the optimum dose of the precipitant, stimulated a rapid flocculation of the silica. After the addition of the precipitation, which is a quarternary ammonium cation, dissolved silica in the form of $H_2SiO_3{}^-$ species rapidly polymerized to form suspended colloidal silica, which flocculated and settled slowly at an alkaline pH. This was attributed to the increasing negative charge at the surface of colloidal silica that facilitated its coagulation with the positive ions of the precipitant in aqueous solutions.

At pH 10.5, the silica concentration in the samples decreased to 18 mg/L after applying 0.1 g/L of FF40 dose. Up to 10.5, where the silica dissolved as silicate, the negatively charged particles attracted the positive charge of the Fennofix precipitants via columbic forces. Therefore, upon collision, their particles aggregated, making the target compound easier for removal.

Unlike in basic conditions, in an acidic environment, the silica particles lack ionic charge. As a result, the SiO_2 polymerization proceeded slowly and aggregation only began after polymeric particles were formed [61]. At pH ranging from 6.5 to 7.5, silica monomer was rapidly converted to particles, which simultaneously aggregated. At pH higher than 7.5, where the dissolution rate of silica is high, its particle growth continued. This finding is in agreement with Gallup et al. [36], who reported that at pH 7.5, the SiO_2 polymerization rate was comparable to that at pH higher than 8.5, while in an acidic pH range, very little SiO_2 polymerized due to the lack of ionic charge.

Overall, pH adjustment to basic conditions (pH 8.5–10.5) significantly improved the silicon removal by the Fennofix precipitants. It is important to note that operating alkaline pH range is not the only solution for combating siliceous scale deposit in TMP pulping process. Water system operators need to take into account the presence of other scaling ions such as Mg^{2+} and Ca^{2+} in the whitewater effluents (Table 3). A pH adjustment to 9.5 or higher results in the precipitation of magnesium silicate if a high concentration of Mg^{2+} is present. In this regard, the resulting precipitant could serve as an efficient flocculant and coagulant aid, promoting a higher silicon removal in the wastewater samples. For this reason, the operating conditions of silicon removal needs to be carefully selected to prevent the solubilization of other precipitated metals in the samples, as most of heavy metals tend to be amphoteric.

3.4. *Effects of zeta potential on Si removal*

Zeta potential controls and facilitates the colloidal suspension of silica in a liquid phase [5]. To optimize silicon removal from the whitewater effluents, changes in the zeta potentials of each sample were determined before and after applying predetermined dose of precipitant.

Fig. 4 presents changes in the zeta potentials after precipitation treatment at varying doses. When the results were plotted, it was observed that the zeta potentials gradually increased with the decreasing SiO_2 concentrations, while the precipitant was increasingly added into the reactor. It was found that changes in the zeta potentials of the treated samples corresponded to the increasing dose of the Fennofix precipitants. In this study, the zeta potentials of the samples lay in the range between −9.5 and −7.1 mV. The agglomeration takes place if their zeta potential ranges from −10 and +10 mV [5]. If changes in the zeta potential are high, the colloidal silica remains dispersed in the suspension. To maximize silicon removal from the samples, the repulsive charges of the precipitant need to be controlled to facilitate the formation of flocs that could settle rapidly in the reactor [62]. The total silica concentration decreased 90% from 200 to 18 mg/L when applying the optimum dose of 0.1 g/L of Fennofix type FF40 and at pH 8.5. However, it was reduced to the point of zero charge at pH 10.5, when most of the target compound in the samples had precipitated.

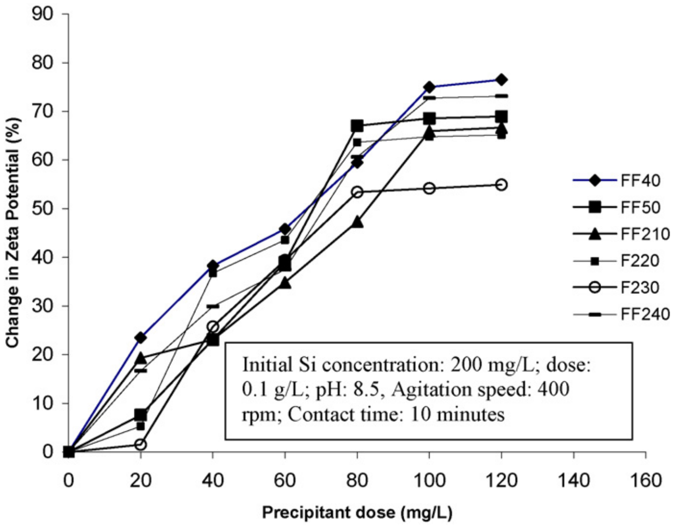

Fig. 4. Changes in zeta potential with an increasing precipitant dose.

3.5. *Integrated chemical precipitation and evaporation*

Due to its ability to recover most of the volume of distillate from highly concentrated flows, evaporation is an important treatment technique to attain zero liquid discharge system. For this reason, treated effluents, resulting from chemical precipitation obtained at optimized conditions, were subsequently treated using evaporation.

During the treatment, the treated samples were concentrated when water as the solvent was vaporized, leaving behind the dissolved silica, while the resulting vapour was vented into the atmosphere or condensed for reuse. Table 5 presents the results of silicon removal after integrating both physico-chemical treatments at 353 K and/or 373 K under a constant pressure of 50,000 Pa and a rotation speed of 30 rpm.

It is observed that about 96% of silicon removal at an initial concentration of 200 mg/L could be attained by applying a higher temperature of 373 K. This result is comparable to those of FF50, which removed 95% of Si at the same temperature. The Si removal at 373 K was slightly higher than that at 353 K, since the higher temperature could dissolve more silica from the samples than the lower one. The combined treatments could generate treated effluents that meet the requirement of maximum discharge standard of less than 50 mg/L set by environmental legislation. For this reason, subsequent biological processes such as activated sludge are not required to complement the removal of silicon from the samples prior to their discharge.

Although the integrated treatment was capable of concentrating and removing silicon from the wastewater effluents, it is costly due to extensive energy consumption during evaporation. However, this drawback may be compensated by its ability not only to improve the treatability of whitewater, but also to remove more silicon from the samples.

In spite of its drawbacks, evaporation has competitive advantages over other conventional physical–chemical processes. This treatment produces a high quality distillate, which can be reused for pulping process. This is an important feature of evaporation, where water conservation is a top priority. Like ion exchange, evaporation can minimize the production of residual waste in the form of sludge and recover valuable materials from wastewater effluents. Therefore, the selection and design of an evaporator system needs to be thoroughly considered for each individual application. The larger is the evaporator, the more costly is the wastewater treatment system. In this regard, reducing the size of an evaporator by pre-concentrating the effluents with membrane filtration may minimize operation and maintenance (O&M) costs in wastewater treatment.

Table 5
Total Si removal by integrated precipitation and evaporation.

Type of precipitant	% Si removal at 353 K		% Si removal at 373 K	
	CP	CP + EV	CP	CP + EV
FF40	91	94	91	96
FF50	90	93	90	95
F210	85	89	85	92
FF210	81	86	81	89
FF220	79	83	79	87
FF230	77	82	77	87
FF240	75	80	75	85

Remarks: CP: chemical precipitation (alone). CP + EV: integrated chemical precipitation and evaporation.

Table 6
Comparison of silicon removal performance using other treatments.

Type of treatment	Operating conditions							Removal efficiency (%)	References
	Precipitant/membrane filtration/adsorbent/oxidant/ electrodes/ion exchanger	Initial SiO_2 concentration (mg/L)	Dose (g/L)	Reaction time (h)	Electric current (A/m^2)	Pressure (bar)	pH		
Individual									
Precipitation	CaO	954	1.5	0.25	–	–	11	93	[5]
	CaO	600	0.5	26	–	–	9.5	73	[36]
	Fennofix type FF40	200	0.1	0.5	–	–	10.5	91	Present study
Coagulation	MgO	140.5	0.8	2	–	–	9	81	[33]
	NaOH	37.3	0.2	0.5	–	–	11	91	[7]
	CaO	37.3	0.15	0.5	–	–	10	68	
Electro-coagulation	Polyaluminium chloride	250	0.03	1.5	10	–	9.5	95	[26]
	Fe^{2+}	200	0.09	1.5	5.7		9.5	90	[20]
Adsorption	$Fe(OH)_3$	50	10	12		–	8.5	71	[22]
Adsorption	Waste Fe(III)/Cr(III)	40	16	0.8	–	–	4–10	95	[23]
Reverse osmosis	DS11	100	–	46	–	24	6.5	96	[1]
	MS19	100	–	46	–	14	6.5	94	
Electro-deionization	NA	1	–	–	4.5	–	7–8	73	[39]
Integrated									
Precipitation and evaporation	Fennofix type FF40	200	0.1	2.5	–	0.5	10.5	96	Present study

3.6. *Comparison of treatment performance between present and other reported studies*

To evaluate the applicability of the integrated evaporation and chemical precipitation for treating TMP whitewater effluents, it is necessary to compare its treatment performance to the results of other treatments in other reported studies. For this reason, a comparative study of various treatments is presented in terms of pH, dose required (g/L), biodegradability, and the initial concentration of SiO_2 (mg/L) in whitewater effluents. Despite having a relative meaning due to different conditions (pH, strength and treatability of the wastewater), this comparison is still useful to evaluate the effectiveness of each treatment for the wastewater.

Table 6 presents the performance of various physico-chemical treatments for silicon removal. Among the various types of treatments, individual treatments are widely employed to remove silicon from TMP whitewater. Treatment such as chemical precipitation using CaO have attained an outstanding silicon removal of over 90% with its COD concentrations ranging from 600 to 950 mg/L. Removal of the same pollutant by electro-kinetic remediation has also received considerable interest [62]. Electrocoagulation and reverse osmosis (RO) have excelled in the silicon removal of over 95% with its concentrations ranging from 100 to 250 mg/L. These results are comparable to those of the chemical precipitation alone in this study, which could accomplish 91% of silicon removal at an initial concentration of 200 mg/L under optimized conditions (dose: 0.1 g/L; pH: 10.5; reaction time: 30 min). Moreover, the integrated evaporation and chemical precipitation could slightly remove more silicon (96%) at the same operating conditions as the individual chemical precipitation treatment.

Even though many techniques can be applied, the key factors in selecting treatment method for the TMP whitewater are its removal performance and treatment cost. In this regard, the characteristics of wastewater effluents from pulp and paper mills need to be carefully considered. In general, the selection of the most suitable treatment for silicon removal depends on the characteristics of whitewater effluents, technical applicability and potential constraints, effluent discharge limit, cost-effectiveness, regulatory requirements, and long-term environmental impacts.

3.7. *Treatment cost analysis for pulp and paper wastewater*

Estimating an accurate cost for the treatment of TMP whitewater, resulting from this preliminary study, is difficult due to the various cost components involved such as pumping equipment and other treatment facilities. In addition, fluctuating changes in the strength of the wastewater samples due to the global market demand on particular types of paper also contribute to the variations of its treatment cost. Therefore, information on the treatment cost of TMP whitewater has rarely been reported in the literature so far (Table 6).

To obtain a reliable estimation of treatment cost for TMP whitewater, a pilot-scale study needs to be carried out. A pilot scale may be more suitable than its corresponding laboratory study to quantify a reliable treatment cost using this integrated treatment. Depending on the size and complexity of the plant, the treatment cost of whitewater varies from one country to another. Even if the pilot study may quantify its treatment cost associated with the combined treatment in this study, a direct comparison of the overall treatment cost of each technique presented in Table 6 is difficult due to their different operating conditions, process employed, and local conditions. Such inconsistency in data presentation makes a cost comparison among the available treatments for TMP whitewater difficult.

4. Concluding remarks

It is evident that both the physico-chemical treatments have been technically applicable and effective to remove silicon from the whitewater effluents. At the same initial SiO_2 concentration of 200 mg/L, 0.10 g/L of dose, and at pH 10.5, the integrated chemical precipitation using Fennofix precipitant type FF40 and evaporation could remove 96% of the target compound. These results are comparable to those of other precipitation using CaO and electro-coagulation in other reported studies, which could accomplish 93% and 95% of silica removal respectively with initial SiO_2 concentrations of 954 and 250 mg/L (Table 6). Both chemical precipitation using FF40 and evaporation could effectively treat a varying strength of TMP whitewater, as their treated effluents could meet the required limit of less than 50 mg/L set by environmental legislation. Therefore, subsequent treatments such as activated sludge are not required to complement silicon removal in the effluents prior to their discharge.

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