

博士論文

Proposal of an Integrated Treatment System for Colored Wastewater and Textile Sludge Derived from Textile Industry Activity

繊維工業から排出される着色排水および汚泥の統合処
理システムの提案

2015年1月

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博士後期課程 環境ソリューション工学専攻

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Summary

The role of textile industry in many developing countries is substantially important in terms of economic and social aspect. In the economic sector, textile industry becomes one of major export commodity particularly in the non-oil and gas sector. More than 50% of export income is coming from either textile or clothing in case of Cambodia, Sri Lanka, Pakistan and Bangladesh. Meanwhile in social aspect textile industry involves many workers, which are able to reduce the problem of unemployment. Apart from the key industry in country development textile industry has a negative impact on the environment especially in case of colored wastewater and sludge. When release to the environment the colored effluent not only become harmful for aquatic biota but also give bad impression from the aesthetic point of view. In addition, some types of dye on colored wastewater contain heavy metals like cobalt, chromium and copper, and resist to biodegradation under the conventional treatment. On the other hand, sludge, a residue from textile wastewater treatment, contains toxic and hazardous materials remaining from textile processing and after textile wastewater treatment. Thus, colored effluent and sludge problems are serious for textile industry management and a development of appropriate treatment system is desired. In this research, I proposed and evaluated an integrated treatment system to solve both colored wastewater and sludge problems through waste utilization and recycling approaches.

Generally textile industry generates two types of wastewater: non-colored wastewater and colored wastewater. In case of a cotton textile processing, non-colored wastewater is coming from the process of desizing, bleaching, mercerizing, etc. while colored wastewater is deriving from dyeing and printing process. The conventional treatment composed of clarification process including coagulation, flocculation, sedimentation and activated sludge system is commonly applied for the treatment of textile wastewater. Unfortunately this process has a disadvantage of generating sludge as a residue, which requires a further treatment for handling.

Chapter I of this thesis described about the waste characteristics derived from textile industry activity as briefly aforementioned on the first and second paragraph.

In chapter II, I discussed about the utilization of textile sludge as a potential adsorbent. I hope the adsorbent can be used to solve the colored wastewater problem through adsorption treatment in the further. The main objective of this research is to investigate the applicability of textile sludge as a potential adsorbent and evaluating its adsorption capacity for color removal treatment. Firstly a simple process called carbonization was conducted to make adsorbents from the sludge. Carbonization is a process to form a carbonaceous material by heat treatment under absent of the oxygen. Textile sludge was heated in electric furnace for 2 hours at the various temperatures from

400 °C to 800 °C. This research demonstrated that the carbonized sludge at 600 °C creating larger specific surface area than other temperatures. Carbonized sludge at 600 °C has 138.9 m²/g of specific surface area. TG-DTA analysis revealed that the organic matter was lost when the textile sludge was heated at 600 °C. Thus, heating over 600 °C was considered as a necessary condition for the production of adsorbent based textile sludge. In addition to improve the specific surface area activated carbon production was also carried out. Physical activation was conducted after carbonized sludge at 500 °C before. Physical activation by carbon dioxide (CO₂) at 900 °C for 30 minutes resulted in 179.9 m²/g of specific surface area. While physical activation by heat steam (H₂O) and nitrogen gas (N₂) at 800 °C for 1 hour created 172.1 m²/g of specific surface area. This research showed that the adsorbent produced through physical activation creates larger specific surface area than only carbonization.

Thus, in order to investigate the performance of textile sludge-based adsorbent for color removal treatment, methylene blue as a representative of cationic dyes and procion brilliant red H-EGXL as a representative of anionic dyes was used in adsorption treatment. The result showed that the carbonized sludge at 600 °C was more suitable for cationic dyes than anionic dyes removal. It has an adsorption capacity of 60.30 mg/g for methylene blue removal and 21.41 mg/g for brilliant red removal. The alkaline pH of adsorbent was also thought to be a dominating factor of the adsorption capacity for the cationic dye. Although the adsorption test using textile sludge-based activated carbon was also performed, the adsorption capacity for both dyes gives no significant difference from that of carbonized sludge. The activated carbon had larger specific surface area, but the carbon content decreased as the result of second heat treatment. The low carbon content of the activated carbon was thought to result in insignificant difference of the adsorption capacity for dyes removal compared with that of the carbonized sludge.

In chapter III the typical gases release from textile sludge combustion were evaluated. This research will give information for the prediction of various gas emissions when textile companies incinerate textile sludge for the sludge treatment. In this research gas emissions were simulated with the MALT (Material-oriented Little Thermodynamic) software and the appropriate combustion temperature was searched to reduce the generation of sulfur oxide (SO_x) and nitrous oxide (NO_x). The component and the volume of textile sludge were modeled on the basis of heavy chemicals used in a dyeing process and a wastewater treatment process, and mass balance of wastewater. The data of heavy chemicals and the water balance were referenced to the case of an actual textile industry in Indonesia. The result showed that the combustion temperature should be carried out lesser than 800 °C to minimize and meet the Indonesian standard regulation for SO_x and NO_x. In this research I also simulated the effect of coagulant species for SO_x generation. The substitute of ferric chloride (FeCl₃) coagulant for aluminum sulfate (Al₂(SO₄)₃) could reduce 18% of SO_x emission at the combustion temperature of 850 °C.

The sludge ash resulted from the combustion treatment causes another problem for solid waste management. In order to tackle this problem, I demonstrated the applicability of textile sludge ash as a clay substitute for brick production in chapter IV. Basically previous researchers have already demonstrated the usability of textile sludge for brick production. However a high addition rate of textile sludge was not able to achieve the first quality standard for compressive strength and water absorption. Preliminary test showed that when the addition of textile sludge ash reached 10%, the brick quality was out from the first quality standard. Furthermore in order to enhance the addition rate of textile sludge on the brick formation without deteriorating the quality, I introduced another material of waste glass into the textile sludge ash-added brick production. The waste glass addition was able to improve the quality of brick. Brick formation with the composition of clay 60%, textile sludge ash 30% and waste glass 10% reached the optimum compressive strength of 73.9 N/mm² and had 5.2 % of water absorption. According to the Japan Industrial Standard *JIS R1250 for common brick*, it achieved the first quality standard. An electron probe micro analyzer (EPMA) and a digital microscope showed that the melted waste glass clogged up the pore formed by sludge ash addition. In addition a leaching test showed that the heavy metal leaching from the brick was strongly inhibited and in the range of the standard regulation. It means that the textile sludge ash-added brick was acceptable in both quality and environmental aspects.

In Chapter V, I discussed the feasibility of textile sludge-based adsorbent for textile wastewater treatment. The mass balance of sludge produced from the textile wastewater treatment processes was estimated on the basis of chemical oxygen demand (COD). In addition, the performance of the sludge-based adsorbent in real wastewater was investigated. Basically the production rate of textile sludge-based adsorbent depends on the generation rate of sludge from the textile wastewater treatment processes. A real restaurant wastewater with 43.8 mg/L of methylene blue was used and treated by the activated sludge process before the adsorption treatment using the textile sludge-based adsorbent. The wastewater had 657 mg/L of total-COD. The activated sludge showed 85.57 % of removal efficiency for COD. According to the half reaction of McCarty the sludge production on this system reached 283.5 mg sludge/ L-wastewater. When the sludge was converted into adsorbent, the final production of adsorbent was estimated to reach 115.2 mg because 59.4% of weight loss was expected during the carbonization at 600 °C. The textile sludge-based adsorbent could remove dyes from the real wastewater with almost no inhibition. I found that the minimum solid/ liquid ratio of adsorbent mass to the volume of wastewater for complete color removal was 0.3 g/L, at which the dissolved-COD removal efficiency reached 40.3 %. Thus, according to the mass balance on this system the utilization of textile sludge-based adsorbent able to solve 38.4% of colored wastewater problem. In order to counter the lack material for colored removal problem, regeneration process of carbonized sludge could be applicable, though 13.8% of adsorption capacity

was lost during second regeneration. In addition, a material adsorbent called synthetic talc has also introduced in this research. Synthetic talc showed a greater ability than carbonized sludge by faster in adsorption equilibrium time and four times higher of adsorption capacity than carbonized sludge for methylene blue removal.

The final conclusion of this research was summarized in chapter VI. An integrated treatment system was proposed for solving the colored wastewater and sludge problems in textile industry through recycling approach. A schematic scene was introduced by the utilization of textile sludge to counter the colored effluent and disposal problem. The conversion of textile sludge into adsorbent for color removal and recycling of textile sludge ash for brick manufacturing was successfully demonstrated and was thought to be a feasible countermeasure to the problems.

論文要旨

多くの発展途上国において、社会経済的観点から繊維産業は極めて重要な役割を果たしており、経済面では、繊維産業は非石油産業部門における主要な輸出品目の一つとなっている。例えば、コロンビアやスリランカ、パキスタン、バングラデシュでは輸出額の50%以上が繊維・衣料製品で占められている。社会面においては、繊維産業は多くの雇用を生み出し、失業問題の軽減に役立っている。しかしながら、国内の重要産業であるという点は別にして、繊維工業の発展は着色排水や染色汚泥の排出に代表されるように、環境に対する負の影響も有している。着色排水が環境中に放出されると、水生生物に悪影響を与えるだけでなく、景観悪化も引き起こす。加えて、着色排水中の一部の染料はコバルトやクロム、銅等の重金属を含有し、従来の排水処理システムでは生分解することが困難である。また、染色排水処理残渣としての汚泥は、染色工程に由来し、染色排水処理後に残存する毒物・有害物質を含んでいる。このように、着色排水や汚泥問題は繊維産業の管理上の深刻な課題となっており、適切な処理システムの構築が望まれている。本研究は、廃棄物の有効利用やリサイクルの手法を導入し、着色排水や汚泥問題を解決するための統合処理システムを提案・評価するものである。

一般に、繊維産業からは2種類の排水が排出される。一つは非着色排水、もう一つは着色排水である。木綿製造過程では、非着色排水は、糊抜き、漂白、マーセル化等の工程から発生する。一方、着色排水は、染色、印刷工程に由来する。通常、染色排水処理には、凝集沈殿処理と活性汚泥処理から構成される処理プロセスが用いられる。しかしながら、この処理プロセスは処理残渣として汚泥が生成するという欠点があり、発生汚泥の処理・処分が必要となる。

第1章では、上記の繊維産業から生成する廃棄物の特性について簡潔にまとめている。

第2章では、将来的に吸着処理を通じて着色排水問題の解決に資することを期待して、吸着剤としての染色汚泥の利用可能性について検討している。この章の主な目的は、吸着剤としての染色汚泥の適用可能性を調査するとともに、着色排水処理のために染色汚泥吸着剤の吸着容量を評価することである。はじめに、炭化と呼ばれる単位操作で染色汚泥から吸着剤を製造した。炭化とは、炭素化合物を酸素非存在下で熱処理するプロセスである。電気炉を用いて、染

色汚泥を 400~800°Cの範囲の様々な温度条件下で 2 時間加熱した。その結果、600°Cで加熱した際に最も大きな比表面積を有する汚泥炭を得ることができた。600°C過熱時の汚泥炭の比表面積は 138.9 m²/g であった。示差熱・熱重量分析 (TG-DTA) の結果、600°Cの加熱により汚泥中の有機物が熱分解されることが明らかとなった。よって、600°C以上の加熱が染色汚泥吸着剤を製造する上での必要条件であると考えられた。比表面積をさらに向上させるため、汚泥炭からの活性炭の生成を試みた。二酸化炭素雰囲気中で 900°C、30 分間の物理的賦活化を行った結果、比表面積は 179.9 m²/g となったが、水蒸気・窒素ガス雰囲気で行った 800°C、1 時間の物理的賦活化では、比表面積は 172.1 m²/g に留まった。このように、炭化の後に物理的賦活化をすることによって、炭化のみよりも高い比表面積を有する吸着剤を生成できることが示された。

次に、染色汚泥吸着剤の色度除去性能を評価するため、陽イオン性染料の代表としてメチレンブルーを、陰イオン性染料の代表として brilliant red H-EGXL を用いて、吸着実験を実施した。その結果、600°Cで生成した汚泥炭が両染料の吸着に最も有効であることが示され、その吸着容量はメチレンブルーに対して 60.30 mg/g, brilliant red に対して 21.41 mg/g であった。吸着剤 pH がアルカリ性であったことが、陽イオン性染料の吸着容量増大の主因であったと考えられた。染色汚泥活性炭を用いた吸着実験も実施したが、汚泥炭と比較して有意な吸着容量の増加は認められなかった。染色汚泥活性炭は高い比表面積を有するが、賦活化処理において炭素含有量が低下していた。よって、活性炭の炭素含有量が低くなったために、大きな比表面積から期待されるような吸着容量の増大効果が得られなかったと考えられた。

第 3 章では、染色汚泥の燃焼過程で放出される典型的なガスを評価した。この研究は、汚泥処理の観点から繊維会社が染色汚泥の焼却処理をした場合を想定し、様々なガス成分の発生予測情報を提供するものである。ここでは MALT (Material-oriented Little Thermodynamic) シミュレーションを実施し、硫黄酸化物 (SO_x) や窒素酸化物 (NO_x) の発生を抑制可能な適切な燃焼温度条件を評価した。染色汚泥の成分や量は、染色工程や排水処理工程で使用される薬剤に基づき、物質収支解析を行うことでモデル化した。薬剤や水量データはインドネシアの繊維産業の実例を参照した。シミュレーションの結果、燃焼温度を 800°C以下としたときに SO_x および NO_x の生成が抑制され、インドネシアの排ガス基準にも適合することが示された。本研究

排水中の染料を除去することが可能であり、共存物質による妨害もほとんど観測されなかった。排水中色度の完全除去に必要な吸着剤の添加率は0.3g/Lと評価された。このとき、溶解性CODも40.3%吸着除去された。このように、このシステムの物質収支解析によれば、染色汚泥吸着剤は着色排水問題の38.4%を解決することができると考えられた。着色排水処理のための吸着剤の不足を解消するため、汚泥炭の再生利用可能性を検討した。その結果、再生処理により13.8%の吸着容量が失われたものの、再生利用可能であることが示された。さらに、別の吸着剤不足解消策として、合成滑石を吸着剤として追加導入することを検討した。合成滑石は汚泥炭よりも吸着速度が大きく、メチレンブルーの吸着容量も約4倍大きかった。また、600℃以上の加熱により吸着容量低下を引き起こすことなく、再利用可能であることが示された。

第6章では、本論文の結論をまとめている。本論文では、繊維産業における着色排水および汚泥処理の問題を解決するために、リサイクル概念に基づく統合処理システムを提案した。このシステムは染色汚泥を資源として有効利用することで着色排水問題や汚泥処分問題を達成するものである。結果として、色度除去のための染色汚泥吸着剤の製造および染色汚泥焼却灰のレンガ製造への再利用が可能であることを実証し、染色排水および染色汚泥問題の実現可能な対策となりうることが示された。

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Chapter I

General Introduction

1.1 The Role of Textile Industry

The textile industry in the world is growing fast together with the increasing of world population. The role of textile industry has significantly important in the economic sector and social sector especially in many developing countries. The textile industry is a strategic industry for the growth and economic development. It is noted that textile and clothing products contribute to the gross domestic product (GDP) of the country, for example 15% in Pakistan, 12% in Cambodia and more than 5% in Srilanka (Keane and Velde, 2008). Whilst in Indonesia, Ministry of Trade and Industry reported that textile together with leather and footwear industry made the fourth largest contributor for GDP with average of 9.44% from 2007 to 2011 as shown on the Table 1.1 (Ministry of Trade and Industry, 2012)

Table 1.1 Sectorial contributions to GDP in Indonesia from manufacture industry
(non-oil and gas sector) from 2007 to 2011 (%)

No	Description	Year				
		2007	2008	2009	2010	2011
1	Food, water and tobacco	29.78	30.38	33.17	33.60	35.23
2	Textile, leather and footwear industry	10.57	9.21	9.21	8.97	9.23
3	Wood product and forestry industry	6.20	6.43	6.33	5.81	5.45
4	Paper and printing	5.13	4.56	4.83	4.74	4.45
5	Fertilizer, chemical and rubber industry	12.48	13.52	12.84	12.73	12.19
6	Cement and mineral excavating industry	3.70	3.61	3.41	3.30	3.25
7	Iron, metal and steel	2.59	2.56	2.13	1.95	2.01
8	Transportation and parts	28.71	28.94	27.33	28.16	27.49
9	Others	0.85	0.78	0.75	0.74	0.72
Total		100	100	100	100	100

From the export commodity, over than 50% of total manufacturing export was dominated

by textile and clothing. In case of Bangladesh and Cambodia that increase to 83.5% and 80%, respectively (Keane and Velde, 2008). In social aspect the textile industry provides opportunities for many jobs. In Indonesia, according to the data from central statistics agency (BPS) in 2012, the textile and textile product (TPT) industry have employed 2.9 million people from micro to large scale industry, or around 21.7 percent from the total labor of non-oil and gas industries (Dewi, 2014). Accordingly, the textile industry plays a major role in the development and industrialization process, not only as a valuable export commodity but also in the social aspect by employing many workers.

1.2 Environmental Problem Derived from Textile Industry Activity

Apart from its beneficial role as growth and industrial development strategies, textile industry discharges numerous wastes to the environment by air pollutants, wastewater, and solid wastes. In case of cotton textile processing, air pollutants emission is derived from the processes like: sizing, desizing, dyeing, scouring and finishing by volatile organic compound, while particulate matter generated from the process of printing and finishing (Babu et al., 2007). Wastewater problems from cotton textile processing especially BOD and COD pollutions are delivered from sizing, desizing, dyeing, printing and finishing process (Babu et al., 2007). The characteristics of textile wastewater from finishing process with different raw fiber are shown on the Table 1.2 (Gitoparmojo and Winiati, 1995). Actually, textile wastewater problems are not only coming from the high concentration of BOD and/or COD, but also from the colored wastewater. Dyeing and printing process consumes large amount of water and released large volumes of wastewater. The characteristics of wastewater from dyeing process are typically rich in color and contain the residue of dyes. Colored effluent without appropriate treatment is actually dangerous if it is released to the environment, especially for aquatic ecosystems. As shown in the Figure 1.1, one case of polluted river caused by colored effluent was found in textile

industry area in Moch Toha district, Indonesia (Photo was taken on December 2014, in different small river at same district).

Table 1.2 Characteristic of wastewater form textile finishing process with different raw fiber in case of textile industry in Indonesia

Characteristic	Unit	Values		
		Cotton	Polyester	Combination fiber (Polyester/rayon, Polyester/cotton)
pH	-	7.9 - 12.5	4.9 - 12.1	5.1 - 12.4
Suspended Solid (SS)	mg/l	160 - 1215	28 - 856	23 - 495
BOD5	mg/l	200 - 864	56 - 1862	57 - 1505
COD	mg/l	438 - 3619	212- 3260	128 - 4584
Phenols	mg/l	0.12 - 0.42	0 - 0.54	0 - 1.88
Oil and grease	mg/l	3.2 - 16.4	6.0 - 72.2	1.2 - 28.4
Total-Chromium	mg/l	0 - 1.42	0 - 1.35	0 - 0.17
Iron (Fe)	mg/l	0.15 - 3.75	0 - 3.00	0.05 - 0.70
Manganese (Mn)	mg/l	0 - 0.10	0 - 2.44	0 - 0.49
Copper (Cu)	mg/l	n.d.	0 - 0.08	n.d.
Zinc (Zn)	mg/l	0 - 0.30	0.02 - 1.00	0 - 0.70
Lead (Pb)	mg/l	n.d.	0-0.11	n.d.

Notes: The characteristic level based on the laboratory test in Indonesian textile research center. While n.d. refers to the no detection

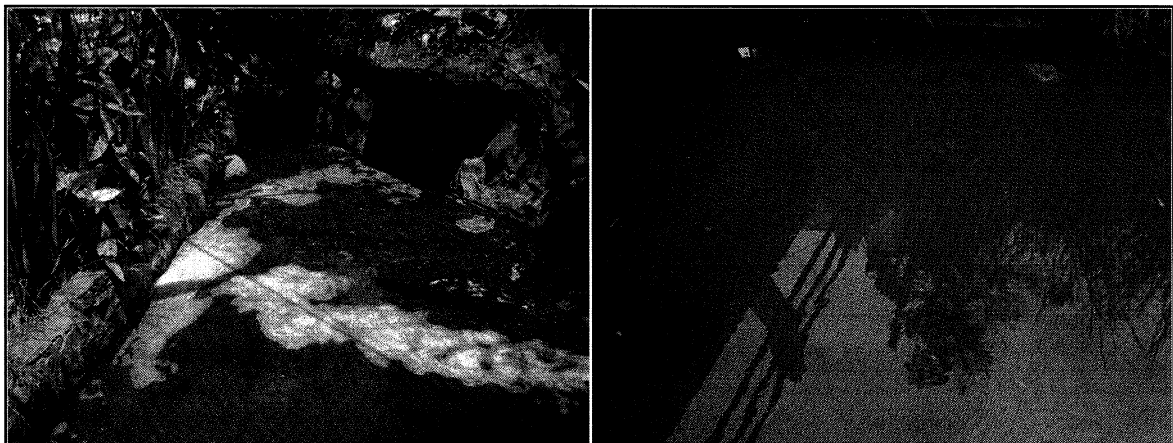


Fig 1.2 The polluted river caused by colored wastewater

In addition depending on the concentration and exposure time dyes may have dangerous

effect on the exposed organism. Dyes may absorb and reflect the sunlight, which can interfere the growth of aquatic plants and bacteria in the water (Slokar and Marechal, 1998). Moreover some dyes contain heavy metals on their chemical structure (Adinew, 2012). In aesthetic point of view dyes on the surface water will easily get attention from the public.

The solid waste problem in case of cotton textile processing is dominated by fiber waste, packaging waste and fabric scraps (Babu et al., 2007). However the solid waste problem from textile industry activity is coming from textile sludge. Textile sludge, a residue from textile wastewater treatment, becomes a problem due to its large amount and volume. Balasubramanain et al. (2006) reported that around 200 ton/days of textile sludge are derived from a common effluent treatment plant in Tripur, India. Rahman and Subari (2008) noted that one company in Indonesia produced 5 ton/month while another company was reported to generate 3 ton/day. European commission directorate general for environment (2001) estimated that around 200 kg of sludge would be produced from each tones of textile material processing. To find an appropriate disposal for huge quantity of sludge becomes a dilemma for textile industry management. In addition textile sludge contains toxic and hazardous materials as a residue from textile processing and wastewater treatment materials.

This research focused on the environmental problems caused by colored wastewater and textile sludge. To find an appropriate treatment for colored wastewater and textile sludge, I proposed an integrated treatment system through recycling approach.

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Chapter II

The Utilization of Textile Sludge as an Adsorbent for Color Removal Treatment

2.1 Introduction

The colored effluent problem from dyeing and printing process of textile industry activity becomes a complex problem to be faced, especially in many developing countries. Many cases, in which textile industry releases the colored effluent without appropriate treatment or even without any treatment, were reported. The colored effluent causes water pollution in the receiving waters. On the other hand, textile sludge, a by-product generated during textile wastewater treatment also causes another problem especially to find appropriate disposal due to its large mass on volume and weight (European commission directorate general for environment, 2001; Balasubramain et al., 2009; Rahman and Subari, 2008). Landfill treatment is one of optional choices but the leachate may cause groundwater pollution due to toxic and hazardous materials belong to the sludge (Schultz and Kjeldsen, 1986). Sludge recycling receives much attention in the recent year due to not only valuable products production but also reduction in the disposal problem. The development of a production technique of a potential adsorbent from textile sludge as a material for solving colored effluent problem was carried out as a basic idea on this research. Previous researches were conducted to investigate the possibility of sludge into adsorbent. For instance, aerobically digested sludge-based activated carbon was successfully produced through physical and chemical activation by Martin et al. (2002). Sludge from urban wastewater treatment and from agrofood industry was converted into potential adsorbent through pyrolysis and combination of pyrolysis and chemical activation (Otero et al., 2003). Moreover Hsiu-Mei et al. (2009) investigated the removal of Orange II and Chrysophenin dyes by adsorbent produced from sludge derived from biological

wastewater treatment of petrochemical industry in Taiwan. According to the previous researches using sludge as a base material, the transformation of textile sludge into potential adsorbent may be possible also. There were many methods to convert sludge into potential adsorbent. Commonly a good adsorbent is determined by larger specific surface area, Smith et al. (2009) reviewed that chemical activation is the suitable method for creating pores on the adsorbent. But, the chemical residue after activation may lead into another problem. For example, the using of zinc chloride ($ZnCl_2$) as a chemical reagent for activation will cause further problem of heavy metal contamination. In this research a simple adsorbent production process called carbonization was conducted. In order to improve the specific surface area, physical activation was also carried out. The final target on this research was to find the appropriate process for sludge-based adsorbent production in order to remove color on the aqueous solution. Potential adsorbent was determined by its ability (adsorption capacity) for color removal treatment.

2.2 Material

2.2.1 Dyes

In this research two types of dye were used as an adsorbate to investigate the possibility of textile sludge-based adsorbent for color removal. Cationic dye was represented by Methylene Blue. Methylene blue trihydrate with the color index of C.I. Basic Blue 9 trihydrate was received from Nacalai Tesque Japan with the chemical formula of $C_{16}H_{18}N_3 \cdot S \cdot Cl \cdot 3H_2O$ and has 373.90 of molecular weight. While the anionic dye was represented by Procion Brilliant Red H-EGXL (obtained from DyStar Japan). Procion Brilliant Red H-EXGL (C.I. Reactive Red 231) has chemical formula of $C_{44}H_{24}Cl_2N_{14}Na_6O_{20}S_6$ and has 1469.98 of molecular weight (World dye variety, 2012). The chemical structures of methylene blue (Molbase, 2013) and brilliant red (World dye variety, 2012) are shown in Figure 2.1.

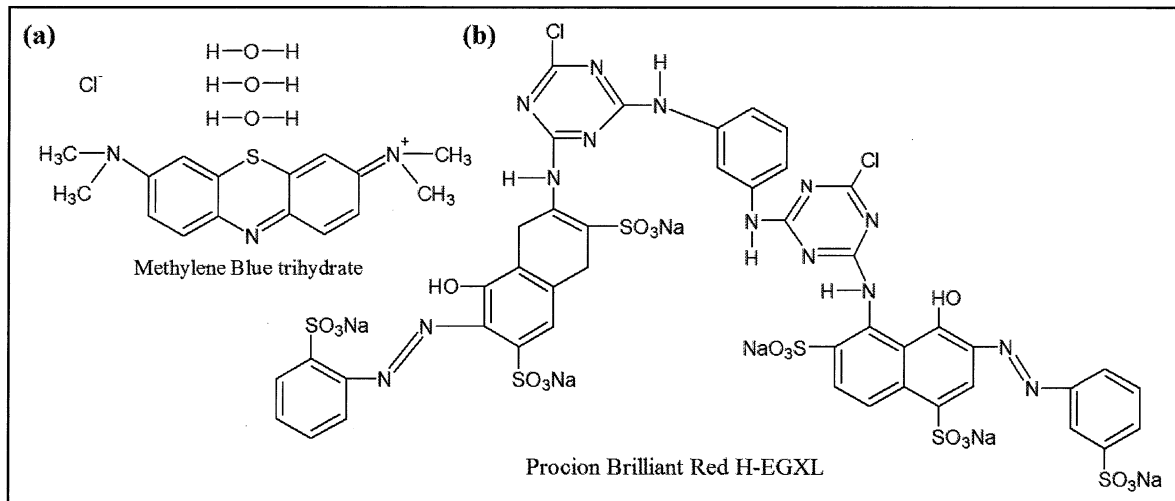


Figure 2.1 Chemical structure of Methylene Blue (a) and Procion Brilliant Red H-EGXL

Both Methylene blue and Brilliant Red powder were firstly dried with drying oven at 105 °C overnight to get a constant weight. Then 1.00 g of each dye was dissolved into deionized water to get 1000 mg/L of stock solution. The stock solution then was diluted again with deionized water to get the necessary concentration for adsorption test. Deionized water for dilution purpose has 0.05×10^{-4} S/m of electrical conductivity.

2.2.2 Textile sludge

Textile sludge was received from a textile company in Wakayama Prefecture, Japan as a by-product from coagulation-flocculation and activated sludge system. Sludge was obtained in a cake form, which was dewatered before. The physical properties of sludge are black color, bad odor and mushy. Dewatered textile sludge contains 77% of water content, 17% of organic matter content and 6% of ash content. The textile sludge (dried base) has 32% of carbon content according to the analyzed with automatic high sensitive NC analyzer type NCH-22F (Sumigraph, Japan). While the chemical composition of textile sludge (ash based) determined with Energy dispersive X-Ray spectrometer type EDX-800HS (Shimadzu, Japan) is shown in Table 2.1.

Table 2.1 Chemical component of textile sludge (ash form)

Component	(%)
SiO ₂	10.6 ± 0.1
TiO ₂	3.2 ± 0.0
Al ₂ O ₃	45.6 ± 0.4
Fe ₂ O ₃	11 ± 0.2
MnO	0.1 ± 0.0
MgO	1.9 ± 0.0
CaO	2.8 ± 0.0
Na ₂ O	12.4 ± 0.4
K ₂ O	1.0 ± 0.0
P ₂ O ₅	3.0 ± 0.0
SO ₃	2.3 ± 0.1

Notes: the sample was triplicated (average data was obtained)

2.3 Experimental Method

2.3.1 Adsorbent production through carbonization

Carbonization is a process of carbon production from organic matter through heating process of material under inert atmosphere (Smith et al, 2009). In the carbonization process the material was prevented from contact with oxygen gas to avoid combustion. The objective of carbonization is to eliminate non-carbon element by thermal decomposition process (Wigman, 1986). In this process textile sludge was placed into iron box and heated with Muffle Furnace F0410 (Yamato, Japan) for 2 hours. The variation of temperature was set from 400 to 800 °C. The experimental setup for carbonization is shown on the Figure 2.2

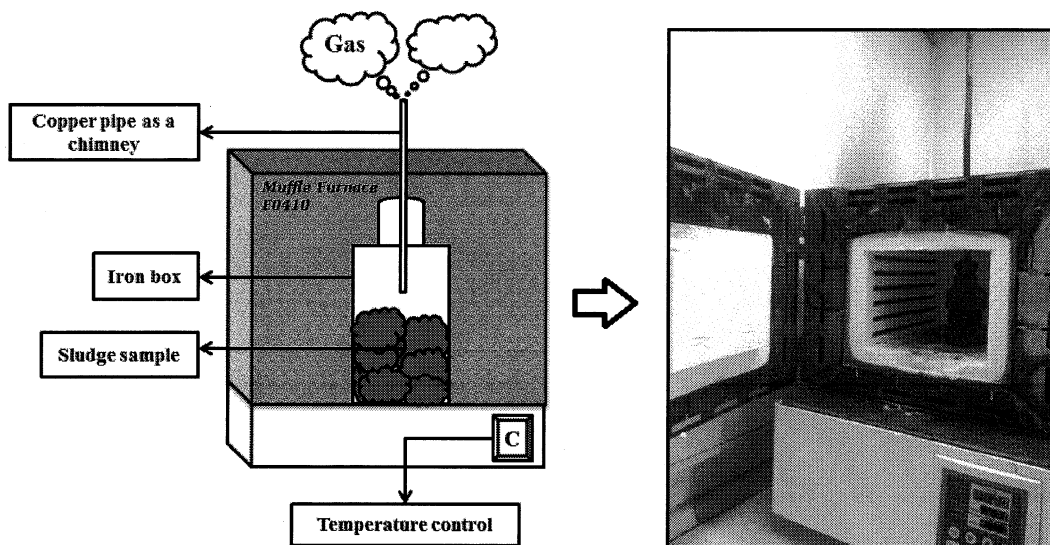


Figure 2.2 Experimental setup of carbonization process

2.3.2 Adsorbent production through physical activation

In order to activate the carbonized sludge, an activation process was carried out. The purpose of this process was to improve the specific surface area of carbonized sludge.

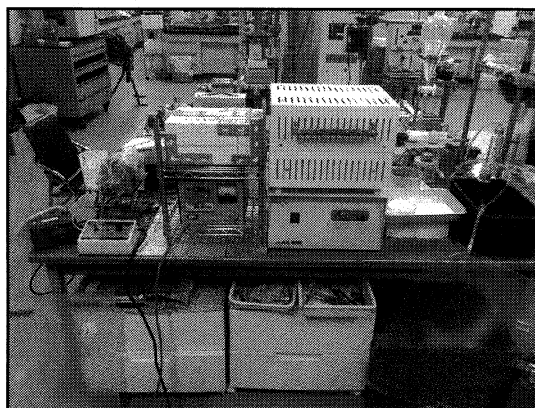
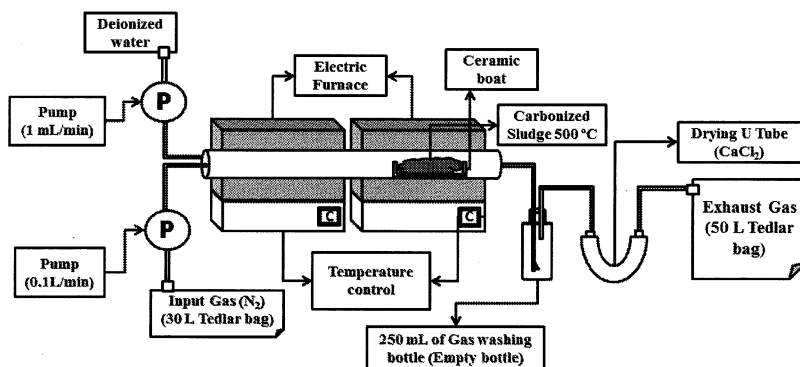


Figure 2.3 Experimental setup of physical activation with steam (H₂O) and nitrogen gas

(N₂)

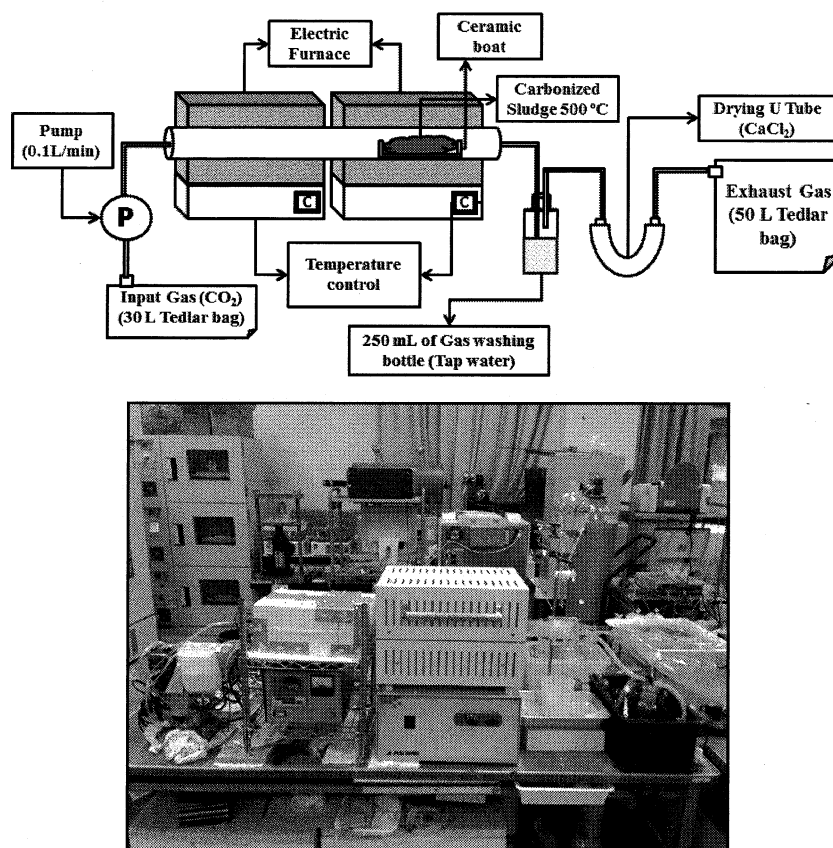


Figure 2.4 Experimental setup of physical activation with carbon dioxide (CO₂) gas

Physical activation was carried out after sludge was carbonized at 500 °C before. It was conducted with two types of gasification. Physical activation with steam (H₂O) combined with nitrogen (N₂) gas and activation by carbon dioxide (CO₂) gas. In (H₂O, N₂) activation the carbonized sludge was heated on the electric furnace at 800 °C for 1 hour. The N₂ gas was flowed at 0.1 L/min together with 1 mL/min deionized water to create the steam. While the physical activation by CO₂ was conducted at 900 °C for 30 minutes. The CO₂ gas was flowed at 0.1 L/min of flow rate. Experimental setups of both physical activations are available on Figure 2.3 and Figure 2.4.

2.3.3 Adsorption experiment

Adsorption experiments were conducted by a batch system. A sample of 0.50 g carbonized sludge with 100 mL dye solution in a 300 mL conical flask were shaken with a

bio-shaking machine, series TB-9R-3F (Takasaki Scientific Instrument Corp., Japan) at 150 rpm at 25 °C. Contact time was varied in the range of 5 to 2560 minutes for methylene blue and in the range of 10 to 5120 minutes for brilliant red in order to clarify the equilibrium time needed. The solution was filtered with 0.1 µm of PES syringe filter (Membrane Solution Co., Ltd) to separate the liquid from solid after the shaking process. The absorbance of filtrate sample then was analyzed with UV-2550 UV-Visible Spectrophotometer (Shimadzu, Japan) at the peak wavelength (λ_{\max} : 665 nm for methylene blue and 535 nm for brilliant red). The identification of residual concentration of dye after adsorption was determined using the calibration curves on Figure 2.5. After determining the residual concentration, the adsorption capacity of adsorbent for color removal was calculated following the equation below (Metcal and Edy, 2003).

$$q_e = \frac{(C_o - C_e)V}{m} \quad (2.1)$$

Where: q_e is the adsorption capacity, the amount of dyes (methylene blue/brilliant red) adsorbed per unit weight of adsorbent (carbonized sludge/ sludge-based activated carbon) (mg/g), C_o is the initial concentration of dye, C_e is the final concentration of dyes after adsorption (mg/L), V is the volume of solution (L) and m is the weight of adsorbent (g).

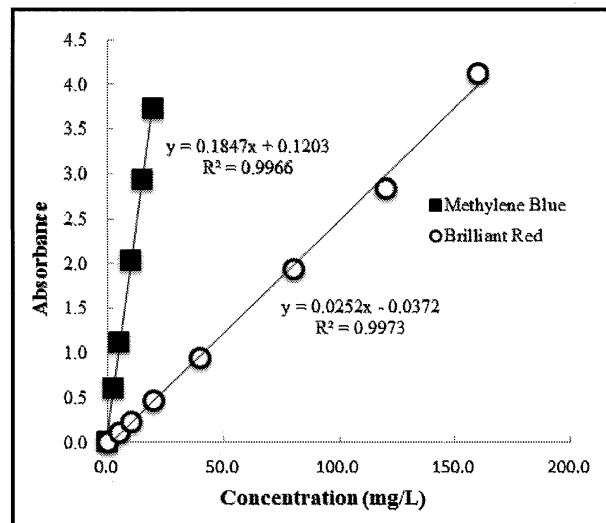


Figure 2.5 Calibration curves of methylene blue and brilliant red

2.4 Result and Discussion

2.4.1 Physical properties of adsorbent produced by carbonization

As shown on the Figure 2.6 the physical appearance of dried textile sludge is actually gray color, however when converted into carbonized sludge the color became black as same with common charcoal. Figure 2.7 shows surface morphology of carbonized sludge at 600 °C on the 5000 magnification with a scanning electron microscope (SEM) JSM-6510 LV series (JEOL, Japan). SEM analysis displayed cavities on adsorbent structure as the result of carbonization.

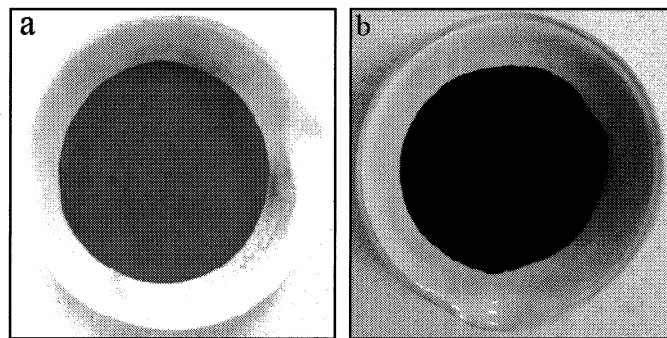


Figure 2.6 Dried textile sludge (a) and carbonized sludge at 600 °C (b)

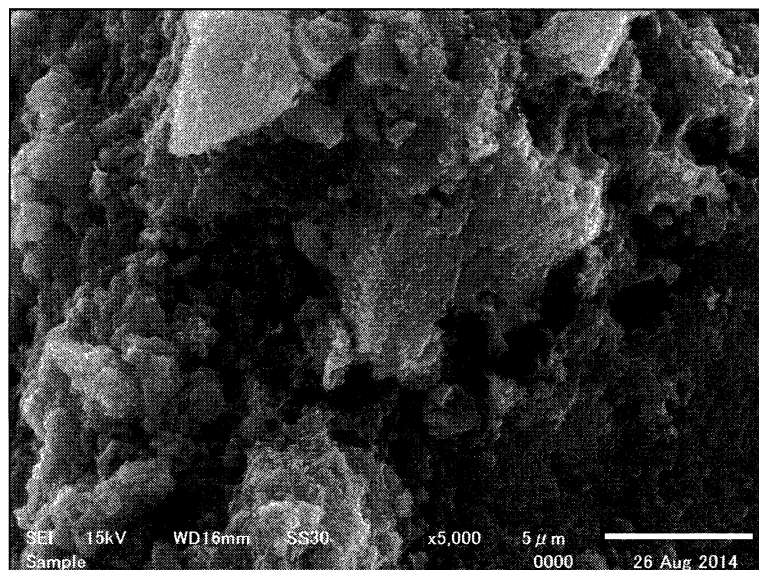


Figure 2.7 SEM picture of carbonized sludge at 600 °C with 5000 magnification

The properties of carbonized sludge with different temperatures are shown on Table 2. Carbon (C) and Nitrogen (N) content was analyzed with automatic high sensitive NC

analyzer type NCH-22F (Sumigraph, Japan). Specific surface area was measured based on Breunauer Emmett Teller (BET) N₂ adsorption method. The pH of carbonized sludge was measured according to the Japan Industrial Standard test method for activated carbon, JIS K1474 (JIS Handbook, 2008). Glass beaker (100 mL) containing adsorbent (1.0 g) with pure water (100 mL) was gently heated at 100 °C for 5 minutes. After cooling, the pH of solution was measured with pH meter (Horiba, Japan). As shown on Table 2 the specific surface area of adsorbent increased with increasing temperature, then reached a plateau after 600 °C. The pH of solution showed the similar pattern, which increased with increasing temperature and stable after 600 °C. Mendez and Gasco (2005) noted that the increasing of pH was related with increasing temperature due to reducing on carboxyl groups belong to the sludge. In order to investigate the thermal behavior of textile sludge with heating treatment, the thermo-gravimetric differential analysis (TG-DTA) was carried out. TG-DTA analysis was performed with TG-DTA 2000 SA (Bruker AXS, Japan). A couple of Al₂O₃ crucibles contained 10±0.3 mg of dried sludge and α-Al₂O₃ (standard sample) was prepared on balance into the machine. The heating temperature was set up until 1200 °C with 10 °C/min of heating rate. Nitrogen (N₂) gas was flowed at 0.3 L/min. Figure 2.8 shows that there were three peaks formed on DTA line as the heating of sludge. Three peaks were detected at 364, 455 and 595 °C, respectively. The weight of sludge on TG line shows that after organic matter was vaporized the weight become stable until the analysis finished. TG-DTA suggested that the complete vaporization of organic matter affected on the stability of surface area especially after 600 °C of carbonization. While Table 2.3 shows the comparison study of carbonized textile sludge with other sludge-based adsorbent on specific surface area.

Table 2.2 Properties of carbonized sludge

Raw sludge	Carbonization temperature (°C)	C (%)	N (%)	BET surface area (m ² /g)	pH	Weight loss (%) (dried base)
1	400	31.1	3.9	76.3	5.8	48.4
2	500	27.2	2.9	97.6	9.4	55.5
3	600	29.7	2.5	138.9	9.8	59.4
4	700	29.6	1.8	137.7	9.8	58.2
5	800	27.4	1.2	136.1	9.9	61.6

Notes: carbonization was conducted for 2 hours for all experiments

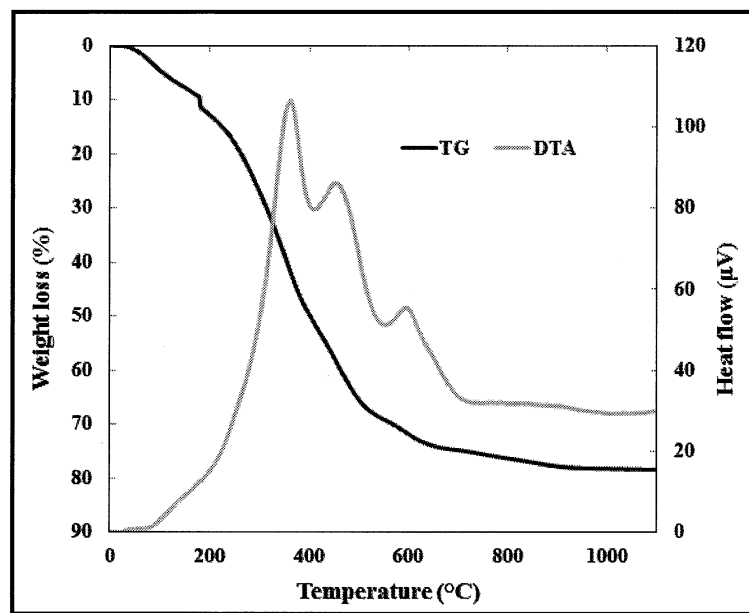


Figure 2.8 TG-DTA of textile sludge (dried base)

Table 2.3 Comparison studies of specific surface area of sludge-based adsorbent

Type of sludge	Carbonization		BET Surface area (m ² /g)	References
	Temperature (°C)	Time (h)		
Anaerobically digested	850	2	100	Lu et al. (1995)
Dewatered municipal	850	2	101	Jeyaseelan and Lu (1996)
Wastewater treatment plant	950	0.5	103	Seredych and Bandosz (2006)
Fertilizer derived from municipal sludge	950	1	122	Bagreev et al. (2001)
Municipal wastewater treatment plant	900	1.17	359	Zhai et al. (2004)
Textile sludge	600	2	138.9	

2.4.2 Physical properties of adsorbent produced by physical activation

On the physical activation, the sample was firstly carbonized at 500 °C (Figure 2.9a) before doing the activation. Ash part appeared on the surface of adsorbent after physical activation (Figure 2.9b). The activated carbon (Figure 2.9c) was obtained after removing of ash part by spatula. Basically it was difficult to completely separate the ash part from the activated carbon. So, remaining ash on the activated carbon was unavoidable. In order to investigate the pore formation, a scanning electron microscope (SEM) analysis was carried out with JSM-6010 LA series (JEOL, Japan) under various magnifications (800, 1500, 5000 and 10,000 M). As shown on the Figure 2.10 and Figure 2.11 micropores were observed on the surface of adsorbent as the result of activation. From the Table 3, I can get information that the physical activation able to improve specific surface area in comparison with base material carbonized sludge at 500 °C (97.6 m²/g). A previous

research conducted by Ikeda and Urabe (2013) shows that physical activation with steam (H_2O , N_2) at $800\text{ }^\circ\text{C}$ resulted highest specific surface area than at 600 and $900\text{ }^\circ\text{C}$ (Table 2.4). On the other hand physical activation by CO_2 at $900\text{ }^\circ\text{C}$ for 30 minutes resulted slightly higher specific surface area than physical activation with steam (H_2O , N_2) at $800\text{ }^\circ\text{C}$. Wigman (1986) mentioned that the higher molecule of CO_2 than H_2O affecting on the higher specific surface area resulted by physical activation with CO_2 .

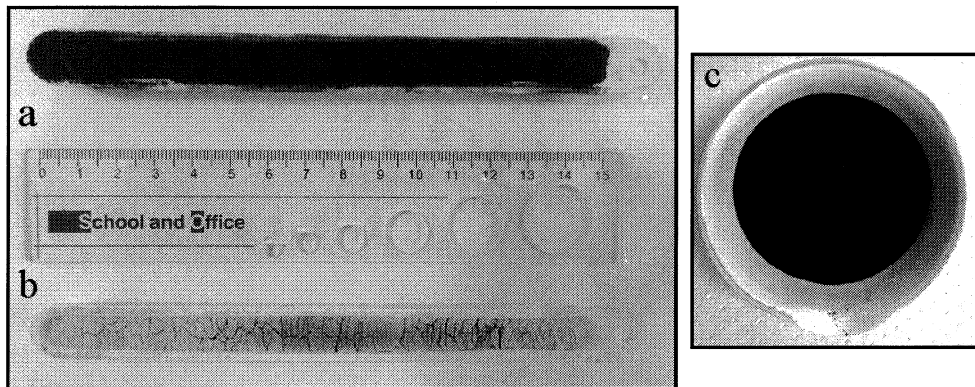


Figure 2.9 Carbonized sludge at $500\text{ }^\circ\text{C}$ (a), activated carbon by physical activation (H_2O , N_2) at $800\text{ }^\circ\text{C}$ for 1h (b), b after removing the ash part of surface (c)

Table 2.4 Properties of textile sludge-based activated carbon

No	Physical activation			C (%)	N (%)	BET Surface area (m^2/g)	pH
	Gasifying gas	Temperature ($^\circ\text{C}$)	Time (h)				
1	N_2 , Steam (H_2O)	600	1	32.9	2.8	150.9	9.5
2	N_2 , Steam (H_2O)	800	1	24.9	1.9	172.1	10.0
3	N_2 , Steam (H_2O)	900	1	15.8	0.7	148.7	9.6
4	CO_2	900	0.5	18.3	0.7	179.9	9.1

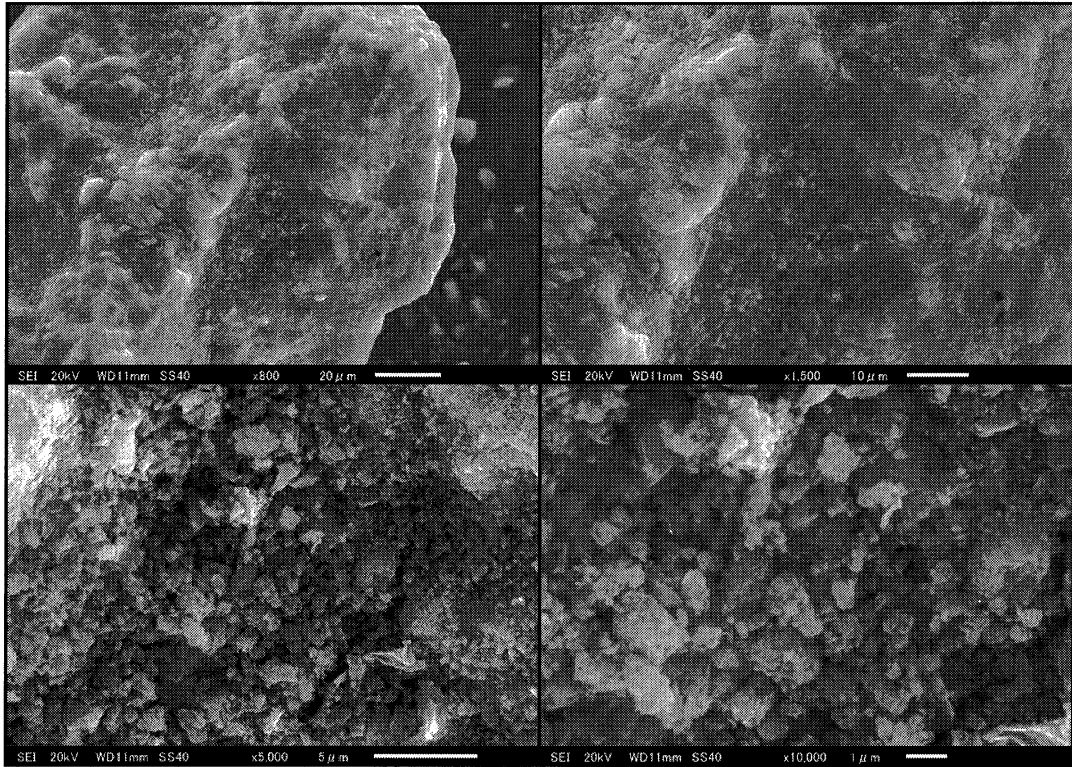


Figure 2.10 SEM picture of activated carbon by physical activation (H₂O, N₂) at 800 °C for 1h with various magnifications

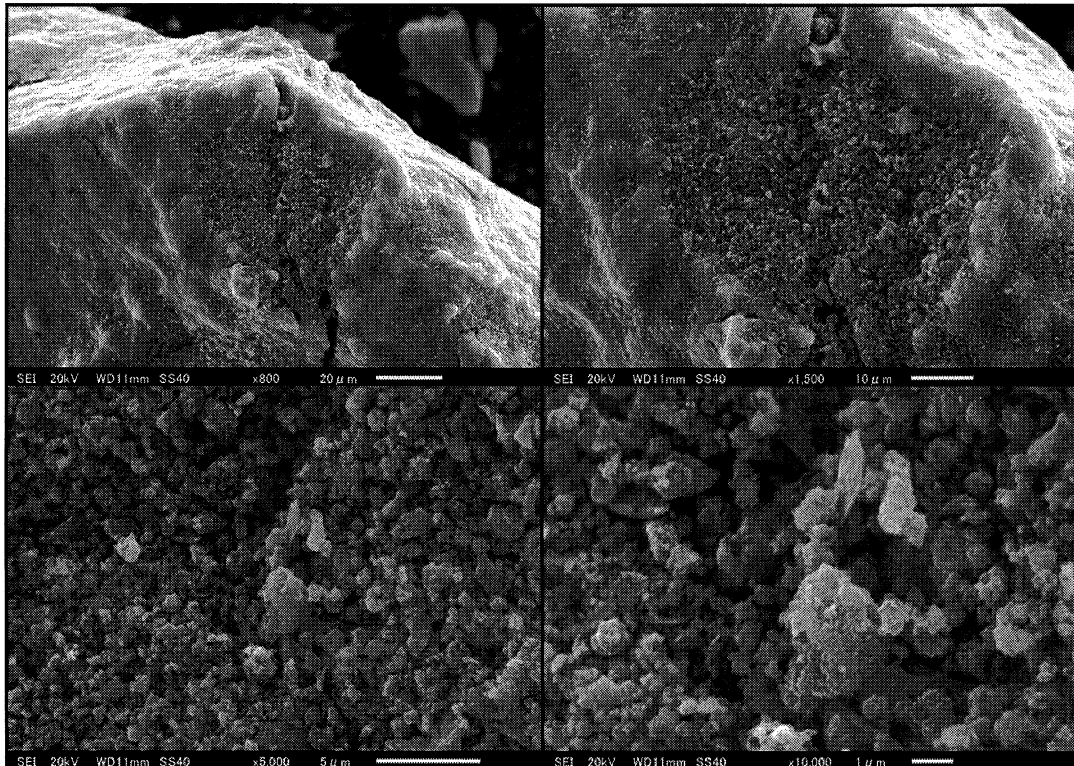


Figure 2.11 SEM picture of activated carbon by physical activation (CO₂) at 900 °C for 30 minutes with various magnifications

2.4.3 Adsorption isotherm of adsorbent produced by carbonization for methylene blue removal

In order to clarify the equilibrium time of adsorption, the effect of contact time was investigated. Equilibrium time is one important point on the adsorption treatment especially to determine the exact contact time for estimation the adsorption capacity of adsorbent. As shown in Figure 2.12 the adsorbent reached the equilibrium after 1280 minutes (21 hours 20 minutes) of adsorption and there was no significance further adsorption after the time. This research suggested that the adsorption of methylene blue into carbonized sludge reached the equilibrium at 1280 minutes.

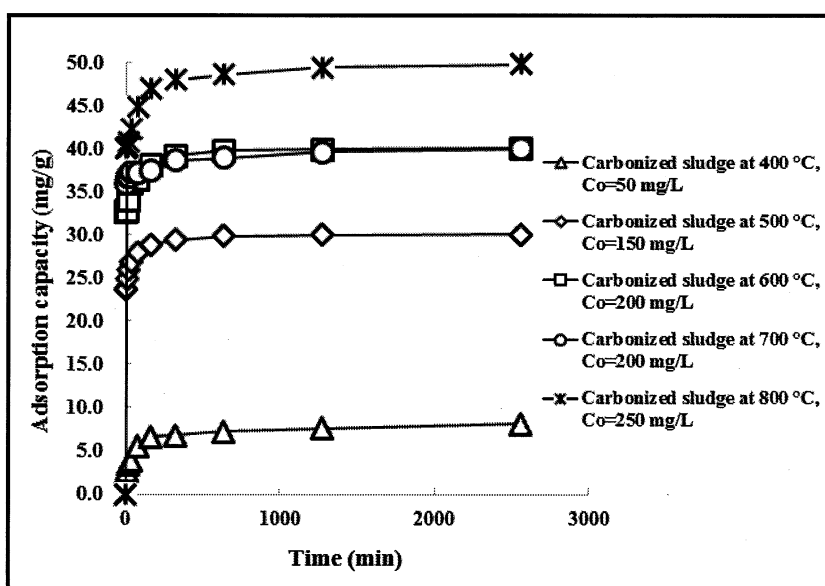


Figure 2.12 Carbonized sludge for methylene blue removal with time variation

In this research, the adsorption isotherm described the dye adsorbed on carbonized sludge as a function of initial dye concentration at the exact of adsorption time, shaking speed, adsorbent mass and constant temperature. Adsorption isotherm of carbonized sludge for methylene blue removal was determined from 30~130 mg/L of initial dye concentration for the carbonization temperature at 400 °C, from 160~260 mg/L for 500 °C, while from 250~350 mg/L for 600, 700 and 800 °C. Figure 2.13 shows the adsorption isotherm graph

as a function of initial dye concentration. Two well-known adsorption isotherms model: Freundlich and Langmuir adsorption isotherms were approached to determine the adsorption mechanism. The Langmuir isotherm model is expressed by the following equation (Langmuir, 1918).

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (2-2)$$

where: q_{\max} is the maximum monolayer capacity of adsorbent (carbonized sludge/sludge-based activated carbon) (mg/g); K_L is the Langmuir capacity factor (L/mg). While the Freundlich adsorption isotherm is as follows (McKay, 1982).

$$q_e = K_f C_e^{1/n} \quad (2-3)$$

where: K_f is the Freundlich capacity factor ($\text{mg.g}^{-1}(\text{L.mg}^{-1})^{1/n}$), and $1/n$ is the Freundlich intensity parameter.

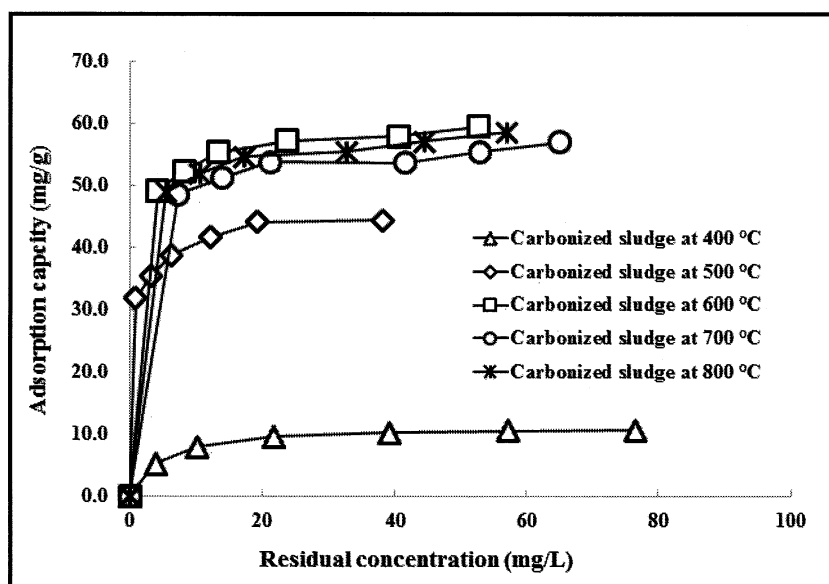


Figure 2.13 Carbonized sludge for methylene blue removal with variation of initial dye concentration

The adsorption isotherm parameter on the Table 2.5 shows that the adsorption of methylene blue onto the carbonized sludge was well fitted to the Langmuir Isotherm model. It was indicated by the comparison of coefficient of determination (R^2) between the Freundlich isotherm and the Langmuir isotherm. The Langmuir isotherm assumes that adsorbate forms a monolayer on the surface of adsorbent (Karadag, 2007), which means that methylene blue molecules formed a monolayer on the surface of carbonized sludge. The maximum capacity (q_{max}) indicated that there was no significant difference of adsorption capacity after the carbonized temperature of 600 °C and higher. Maximum capacity of carbonization at 600 °C reached 60.30 mg/g that means for 1 g of carbonized sludge of 600 °C to maximally uptake 60.30 mg of methylene blue from the solution. The adsorption process is basically controlled by many factors including specific surface area and pH of adsorbent. As aforementioned, the specific surface area reached a plateau after 600 °C of carbonization. It answered the reason why the adsorption capacity after 600 °C of carbonization was not changed.

Table 2.5 Isotherm parameter of carbonized sludge for methylene blue removal

Adsorbent (Carbonized sludge)	Freundlich Isotherm Parameter			Langmuir Isotherm Parameter		
	1/n	K_f (mg/g)(L/mg) ^{1/n}	R^2	q_{max} (mg/g)	K_L (L/mg)	R^2
at 400 °C	0.226	4.33	0.862	11.26	0.258	0.997
at 500 °C	0.095	32.33	0.968	45.25	1.319	0.998
at 600 °C	0.072	44.97	0.944	60.30	0.851	1.000
at 700 °C	0.065	43.09	0.921	57.91	0.569	0.999
at 800 °C	0.073	43.57	0.972	59.57	0.623	1.000

Notes: the sample was triplicated (average data was obtained)

In addition the adsorption of cationic dye is actually more suitable with alkaline pH than acidic pH condition. It is a reason why the carbonization at 400 °C has low adsorption capacity, which resulted in not only smaller in specific surface area but also lower pH

compared than carbonized sludge with higher carbonization temperature. This research deduced 600 °C was a suitable temperature in case of adsorbent production through carbonization for methylene blue removal.

2.4.4 Adsorption isotherm of adsorbent produced by carbonization for brilliant red removal

The removal performance of carbonized sludge for adsorbing anionic dye was also investigated in this research. The adsorption times on Figure 2.14 shows that carbonized sludge need more time for taking brilliant red than methylene blue; 2560 minutes (42 hours 40 minutes) to reach the equilibrium. Based on the equilibrium time, the effect of initial dye concentration was determined. The adsorption experiments were set up from 40 to 140 mg/L for carbonized sludge at 500 to 800 °C. In case of 400 °C initial dye concentration was determined by 200 to 300 mg/L. The result of adsorption experiments as the effect of initial dye concentration is shown on Figure 2.15. Although the initial dye concentration for carbonized sludge at 400 °C was set at the higher concentration than others, the residual concentration resulted in lower concentration, which are equivalent to the higher adsorption capacity.

Table 2.6 Isotherm parameter of carbonized sludge for brilliant red removal

Adsorbent (Carbonized sludge)	Freundlich Isotherm Parameter			Langmuir Isotherm Parameter		
	1/n	K_f (mg/g)(L/mg) ^{1/n}	R ²	q_{max} (mg/g)	K_L (L/mg)	R ²
at 400 °C	0.065	36.77	0.838	49.09	0.664	0.998
at 500 °C	0.267	6.34	0.993	19.31	0.185	0.991
at 600 °C	0.346	4.96	0.989	21.41	0.117	0.989
at 700 °C	0.406	3.88	0.994	22.46	0.078	0.978
at 800 °C	0.397	4.42	0.994	23.64	0.094	0.986

Notes: the sample was triplicated (average data was obtained)

Adsorption isotherm parameter (R^2) shows that the adsorption mechanism was expressed by both the Freundlich and Langmuir isotherms. As shown on Table 2.6 the highest maximum adsorption capacity was reached by carbonized sludge at 400 °C for 49.09 mg/g.

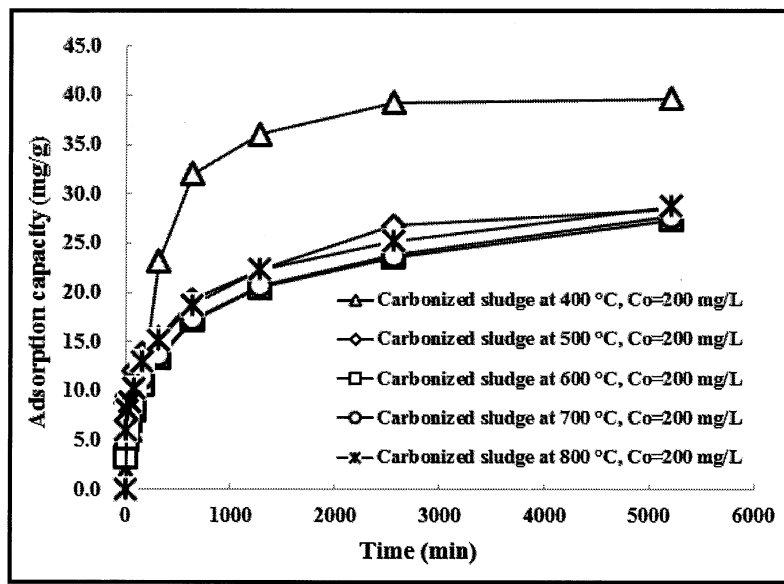


Figure 2.14 Carbonized sludge for brilliant red removal with adsorption time variation

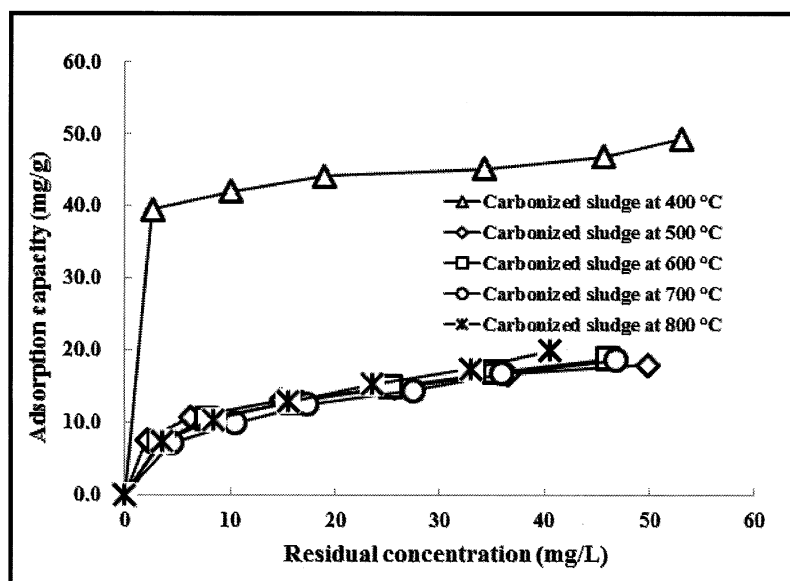


Figure 2.15 Carbonized sludge for brilliant red removal with variation of initial dye concentration

The adsorption capacity of carbonized sludge from 500 to 800 °C did not show significant difference from each other. This research deduced that pH of adsorbent has a more important role than specific surface area for brilliant red removal. Table 2.2 shows that pH of carbonized sludge at 400 °C was 5.8 but from 500 to 800 °C of carbonization all pH was higher than 9. The characteristic of anionic dye, which prefers acidic condition to alkaline condition was suggested as the reason for the higher adsorption capacity of carbonized sludge at 400 °C.

2.4.5 Adsorption isotherm of adsorbent produced by physical activation for methylene blue and brilliant red removal

The previous research mentioned that the physical activation was able to improve the specific surface area of carbonized sludge. In this section, the adsorption capacity of textile sludge-based activated carbon by CO₂ at 900 °C for 30 minutes and by H₂O, N₂ at 800 °C for 1h was investigated. Figure 2.16 demonstrates that the sludge-based activated carbon reached the equilibrium at 1280 minutes for methylene blue removal and 2560 minutes for brilliant red removal. In order to investigate the maximum adsorption capacity, the effect of initial dye concentration was also observed at the equilibrium time. Dye concentration ranged from 180 to 280 mg/L for methylene blue and 40 to 240 mg/L for brilliant red. The result of the effect of dye concentration is shown on the Figure 2.17 and Table 2.7. Although there was no significant difference on maximum capacity between activated carbon by CO₂ and by H₂O, N₂ for both methylene blue and brilliant red removal. It seems that activated carbon by H₂O, N₂ is more suitable for methylene blue removal due to has higher pH of adsorbent while activated carbon by CO₂ is good for brilliant red due to the lower pH of adsorbent. It was thought to affect the slight difference in maximum capacity.

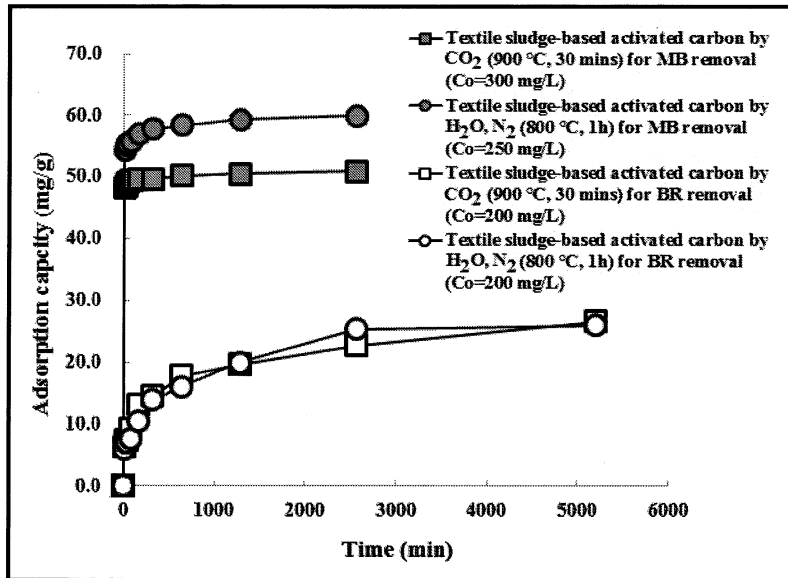


Figure 2.16 Activated carbon based textile sludge for methylene blue (MB) and brilliant red (BR) removal with adsorption time variation

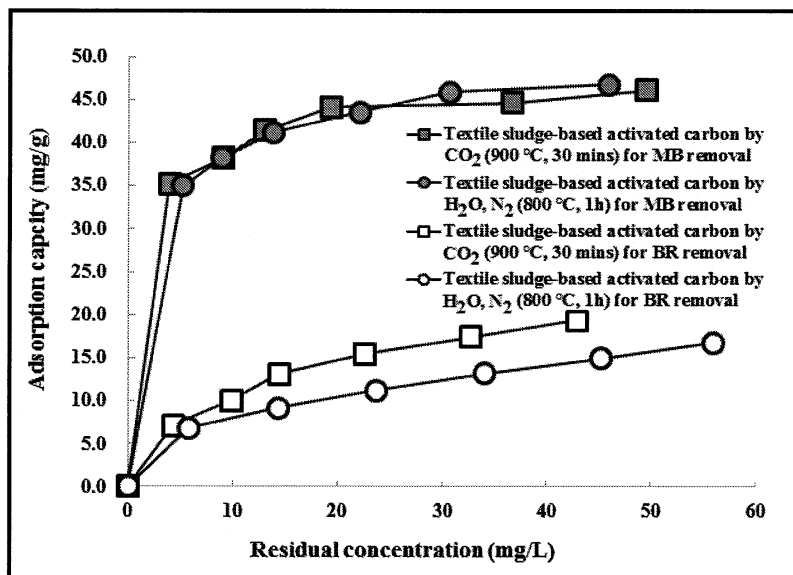


Figure 2.17 Activated carbon based textile sludge for MB and BR removal with variation of initial dye concentration

However if comparing with the maximum capacity of carbonized sludge the adsorption capacity of sludge-based activated carbon was not good. The decrease in carbon content of sludge-based activated carbon was supposed to be the factor in lower adsorption capacity

even though sludge-based activated carbon had greater specific surface area. For example, in case of methylene blue removal: carbonized sludge at 600 °C has 138.9 m²/g of surface area, 29.7% of carbon content and 60.30 mg/g of maximum capacity, while sludge-based activated carbon by CO₂ at 900 °C for 30 minutes has 179.9 m²/g of surface area, 18.3% of carbon content and 47.39 mg/g of maximum capacity. The difference on carbon content was thought to be an important role in the maximum capacity of adsorbent.

Table 2.7 Isotherm parameter of textile sludge-based activated carbon for MB and BR removal

Adsorbent (Textile sludge-based activated carbon)	Freundlich Isotherm Parameter			Langmuir Isotherm Parameter		
	1/n	K _f (mg/g)(L/mg) ^{1/n}	R ²	q _{max} (mg/g)	K _L (L/mg)	R ²
by CO ₂ (900 °C, 30 mins) for MB removal	0.106	30.88	0.924	47.39	0.574	0.999
by H ₂ O, N ₂ (800 °C, 1h) for MB removal	0.137	28.35	0.972	49.21	0.410	0.998
by CO ₂ (900 °C, 30 mins) for BR removal	0.428	3.97	0.962	24.23	0.083	0.966
by H ₂ O, N ₂ (800 °C, 1h) for BR removal	0.393	3.34	0.984	20.61	0.061	0.977

Notes: the sample was triplicated (average data was obtained)

2.5 Conclusion

The textile sludge was successfully converted into a potential adsorbent. Carbonization at the heating temperature of 600 °C and higher resulted in a constant specific surface. TG-DTA revealed that the constant specific surface area was realized by volarization of organic matter at 595 °C. The carbonized sludge at 600 °C itself has 138.9 m²/g of specific surface area. In addition, physical activation was able to improve the specific surface area; the sludge-based activated carbon by H₂O and N₂ at 800 °C for 1h enhanced the specific surface area to 172.1 m²/g and sludge-based activated carbon by CO₂

at 900 °C for 30 minutes to 179.9 m²/g from the base sample of carbonized sludge at 500 °C (97.6 m²/g). The adsorption treatment was also performed for methylene blue and brilliant red removal. In case of carbonized sludge, carbonized sludge at 600 °C was recommended for methylene blue removal while brilliant red removal was suitable with carbonized sludge at 400 °C. On the contrary, the adsorption capacity of sludge-based activated carbon did not give better result compared with carbonized sludge. Although the activated carbon had larger specific surface area, the decrease in carbon content was thought to be a factor of low adsorption capacity. Thus, I supposed that carbonization is an appropriate method for converting textile sludge into potential adsorbent, because it is not only a simple process with good ability in color removal but also in terms of low energy consumption compared with physical activation.

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Chapter III

Flue Gas Analysis Simulation of Textile Sludge Combustion

3.1 Introduction

Incineration process involving combustion treatment is frequently applied to sludge in order to reduce the volume and weight. In addition the ability of the heat treatment for the elimination of toxicity of sludge becomes another benefit of this process (United States Environmental Protection Agency (EPA), 2006). Moreover an energy recovery from the waste also can be obtained from incineration. Apart from its advantages incineration also has a disadvantage of releasing various type of gases, particulate matter, volatile organic compounds (VOC), furan, dioxin and other dangerous gaseous species (EPA, 2006). The emission from incineration is strictly monitored by standard regulations. Actually the emission from incineration is depended on the characteristics of waste and incineration itself (EPA, 2006). In the textile waste, textile sludge characteristic actually depends on the various chemicals involved in textile wastewater and used in a typical textile wastewater treatment, while contaminants in the textile wastewater depend on the chemical species used in the textile processing. In textile processing especially in dyeing and printing processes, the dyeing recipe has a significant role to determine the characteristics of wastewater. On the other hand conventional treatments consist of clarification treatments (coagulation, flocculation and sedimentation) combine with an activated sludge treatment often used for the textile wastewater treatment. Generally the clarification process has a function to remove color and suspended solids, which divided into coagulation, flocculation and sedimentation. The coagulant, a material of coagulation, has a role for the destabilizing particles, the flocculant, a material of flocculation, then make a bigger floc (Metcalf and Edy, 2003). Finally the bigger floc will be settled on the sedimentation tank through gravitation. The settled floc then becomes chemical sludge.

Smith (2009) explained that sewage sludge generally contains: sludge from a primary sedimentation tank, biological sludge as a residue of excess sludge from an activated sludge treatment and in addition to chemical sludge from a clarification process. In this research, I determined a textile sludge composition based on the mass balance of wastewater, chemicals used on dyeing recipe, components of wastewater treatment including coagulant, flocculant and activated sludge. The textile sludge composition then simulated for burning into various temperatures. The objective of this chapter is to identify typical gas emission with its concentration from the textile sludge combustion as the function of temperature. The simulation was carried out by using Material Oriented Little Thermodynamic (MALT) software. I also simulated the influence on coagulant species for flue gas generation.

3.2 Material Input for Simulation

3.2.1 *Textile wastewater treatment flow*

The wastewater flow and data were referenced to the case study in a textile industry in Indonesia (Herlambang, 2010). The wastewater was separated into colored wastewater and uncolored wastewater. Firstly colored wastewater goes to the clarification process A. Coagulant Iron (II) sulfate (FeSO_4) has a function to remove the color, Lime (CaO) has a function to increase the pH, while Polymer ANP-10 was added as an function to accelerate the sedimentation process as a flocculant. After the treatment of colored wastewater, the wastewater then goes to the activated sludge system for biological treatment. In this system the wastewater was mixed with uncolored wastewater. Furthermore the advance treatment of clarification B was applied for suspended solids and other contaminants removal by addition of coagulant aluminum sulfate $\text{Al}_2(\text{SO}_4)_3$ and flocculant ANP-10 before release to the environment. Finally the sludge from the clarification processes A, B and the activated sludge process was collected in the Final

sludge tank. The wastewater flow is shown on the Figure 3.1

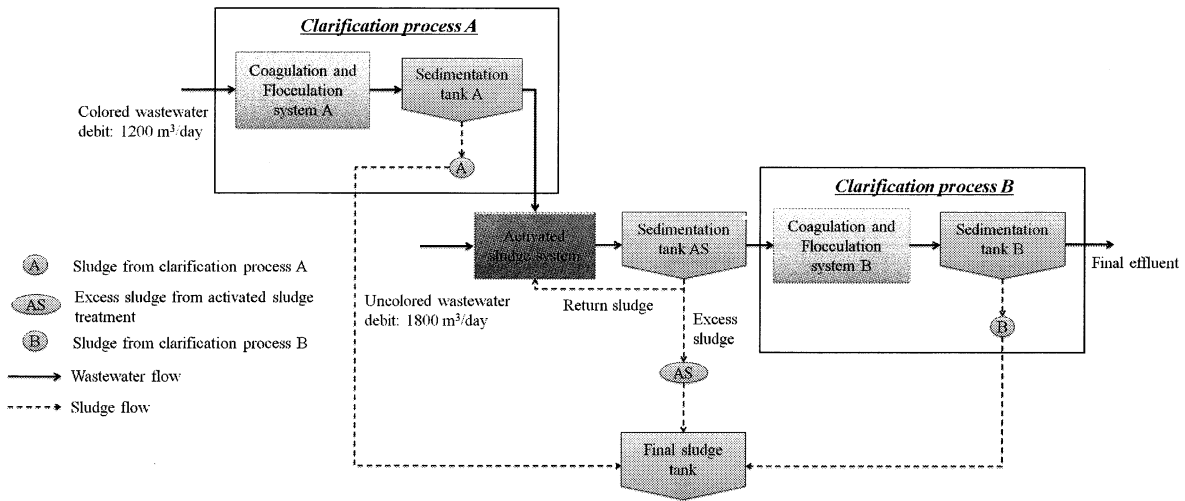


Figure 3.1 Typical textile wastewater treatments

3.2.2 Wastewater and activated sludge component

The components of textile wastewater and chemical doses for textile wastewater treatment are summarized in Table 3.1. Roanne (2010) while the chemical used for textile wastewater treatment was referenced to a case study in one of textile industries in Indonesia (Herlambang, 2010). On the other hand the activated sludge data were obtained from a literature (Metcalf and Edy, 2013) while the chemical composition data of activated sludge were obtained from laboratory analysis. The cell composition of bacteria on activated sludge was based on that of prokaryote cells (Metcalf and Edy, 2013). The chemical composition analysis of a real activated sludge sample from municipal wastewater treatment in Shiga Prefecture was performed with an energy dispersive X-Ray spectrometer type EDX-800HS (Shimadzu, Japan). The cell composition is shown on Table 3.2, whilst Table 3.3 shows the chemical composition.

Table 3.1 Textile wastewater and wastewater treatment component

(a) Wastewater component			
		Component	Amount
		Colored wastewater	Material
Sodium chloride (NaCl)	32,691 kg/day		
Sodium carbonate (Na ₂ CO ₃)	2,960 kg/day		
Detergent (C ₁₂ H ₂₅ NaO ₄ S)	2,018 kg/day		
Condition	Initial COD concentration		432 mg/L
	Discharge wastewater	1,200 m ³ /day	
Uncolored wastewater		Initial COD concentration	679 mg/L
		Discharge wastewater	1,800 m ³ /day
(b) Chemical dose for textile wastewater treatment			
Clarification process A	Coagulant (FeSO ₄)		780 kg/day
	Lime (CaO)		270 kg/day
	Flocculant (Polymer ANP-10)		0.6 kg/day
Clarification process B	Coagulant (Al ₂ (SO ₄) ₃)		675 kg/day
	Flocculant (Polymer ANP-10)		1.5 kg/day
Activated Sludge (C₅H₇O₂N)			12,000 kg/day

The colored wastewater components were referenced to the dyeing recipe by

Table 3.2 Composition of cell based elemental formation

Elements	Percent weight on dried base (%)	Ratio
Carbon (C)	50.0	0.53
Hydrogen (H)	9.0	0.10
Oxygen (O)	22.0	0.23
Nitrogen (N)	12.0	0.13
Sulfur (S)	1.0	0.01
Chlorine (Cl)	0.5	0.01

Table 3.3 Chemical composition of activated sludge (ash form)

Component	Dried base (%)	Component	Dried base (%)
SiO ₂	11.5	P ₂ O ₅	44.9
TiO ₂	0.3	SO ₃	0.3
Al ₂ O ₃	6.1	Cl	0.0
Fe ₂ O ₃	2.1	Cr	0.0
MnO	0.1	Ni	0.1
MgO	5.0	Cu	1.7
CaO	8.5	Zn	1.0
Na ₂ O	4.9	Pb	0.1
K ₂ O	13.6	Total	100.0

Accordingly, the activated sludge data were calculated according to the necessary amount of activated sludge per day. Dried activated sludge was known to have 92% of combustible matter and 8% of ash content. Table 3.4 shows the daily production of each component in activated sludge.

Table 3.4 Daily productions of components in activated sludge

Mass ratio	Component	(%)	Ratio	Daily production (kg/day)	Total production (kg/day)
Combustible matter (0.92)	C	52.9	0.487	5841.3	11,040
	H	9.5	0.088	1051.4	
	O	23.3	0.214	2570.2	
	N	12.7	0.117	1401.9	
	Volatile S	1.1	0.010	116.8	
	Volatile Cl	0.5	0.005	58.4	
	Total	100.0	0.920		
Ash content (0.08)	SiO ₂	11.5	0.009	110.4	960
	TiO ₂	0.3	0.000	3.2	
	Al ₂ O ₃	6.1	0.005	58.1	
	Fe ₂ O ₃	2.1	0.002	20.1	
	MnO	0.1	0.000	0.5	
	MgO	5.0	0.004	48.5	
	CaO	8.5	0.007	81.1	
	Na ₂ O	4.9	0.004	46.6	
	K ₂ O	13.6	0.011	130.1	
	P ₂ O ₅	44.9	0.036	431.5	
	SO ₃	0.3	0.000	2.4	
	Cl	0.0	0.000	0.0	
	Cr	0.0	0.000	0.2	
	Ni	0.1	0.000	0.7	
	Cu	1.7	0.001	16.6	
	Zn	1.0	0.001	9.2	
Pb	0.1	0.000	0.7		
Total	100.0	0.080		12,000	

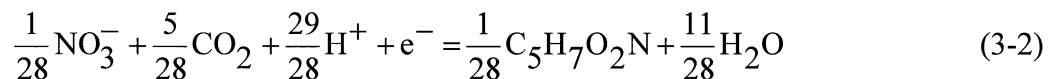
3.2.3 The estimation of sludge production

In this section I tried to estimate the sludge production based on the COD removal efficiency for each wastewater treatment process. According to the wastewater flow on Fig. 3.1 that involves three processes Clarification process A, Activated sludge system and Clarification process B. The clarification process A has a function for color removal

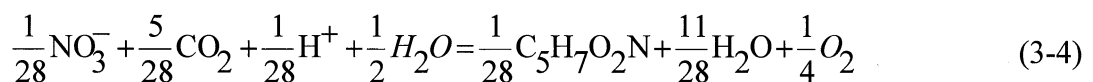
treatment through coagulation and flocculation. The colored wastewater discharge is 1200 m³/day with COD of 432 mg/L. This process has 74% of COD removal efficiency. According to the data above, the amount of sludge production was estimated following the equation below:

$$SP = (COD_{input} \times IL) - (COD_{output} \times EL) \quad (3-1)$$

where, SP is sludge production per day (g/day), COD_{input} is the COD before conducting treatment (g/m³), IL is influent loading of wastewater (m³/day), EL is effluent loading of wastewater (m³/day), COD_{output} is the COD after conducting treatment (g/m³). Following the calculation, the sludge production from clarification process A was estimated to be 384 kg/day. After the color removal treatment the wastewater then mixed with uncolored wastewater for biological treatment with activated sludge system. McCarty (1975) reported that the production of activated sludge can be estimated by the COD, organic nitrogen and organic carbon contents. In this section the sludge production from activated sludge system was only determined by COD removal efficiency according to the half reactions (McCarty, 1975).



The equation (3-4) could be obtained from equation (3-2) and equation (3-3).



If refer to equation (3-4), it can be known that 1 mole of C₅H₇O₂N consumes 7 moles of O₂. It means to convert COD into weight of activated sludge need conversion factor of 113/224. Thus the sludge production from activated sludge system can be calculated by equation (3-5).

$$SP^* = \left[(COD_{input} \times IL) - (COD_{output} \times EL) \right] \times \frac{113}{224} \quad (3-5)$$

Where SP^* is sludge production from activated sludge treatment. The sludge around 69.3 kg/day can be obtained from the activated sludge process due to 10% of removal efficiency. The advance treatment of clarification process B has a role for suspended solids and other contaminants removal, with COD removal efficiency of 46%, the sludge production is 561 kg/day. Therefore, the total sludge production from this wastewater treatment system is around 1.01 ton/day as noted on Table 3.5.

Table 3.5 Sludge production based COD removal ratio for each treatment method

Treatment method	Wastewater	COD inlet (mg/L)	COD outlet (mg/L)	Removal efficiency (%)	Sludge production (kg/day)
Clarification process A	Colored	432	112	74	384
Activated sludge	Colored	112	406	10	69.3
	Uncolored	679			
Clarification process B	Mixed	406	219	46	561
Total					1,014

3.2.4 Textile sludge model

Textile sludge formation was modeled based on the mass balance of wastewater, the composition of dyeing recipe, materials for wastewater treatment and the production of activated sludge. Table 3.6 shows the initial input for the MALT simulation. The sludge was assumed to be around 60% of water content after dewatering process and drying. The proportion of dissolved components like sodium chloride (NaCl) was mentioned to the dewatering process of sludge. It means that the dissolved components are allocated to the dewatering effluent and the sludge according to the water volume ratio.

Table 3.6 Modeled textile sludge

Component	Composition (%)
Water content	60.039
Combustible matter	34.162
C	18.029
H	3.229
O	7.937
N	4.291
Volatile S	0.458
Volatile Cl	0.219
Ash content	5.799
SiO ₂	0.333
Al ₂ O ₃	0.175
Fe ₂ O ₃	0.060
CaO	0.244
Na ₂ O	0.178
K ₂ O	0.392
P ₂ O ₅	1.300
SO ₃	0.007
Cu	0.050
Zn	0.028
Pb	0.002
Sodium chloride (NaCl)	1.458
Sodium carbonate (Na ₂ CO ₃)	0.891
Coagulant (FeSO ₄)	0.235
Lime (CaO)	0.001
Coagulant (Al ₂ (SO ₄) ₃)	0.203

3.2.5 Textile sludge model with difference coagulant used

In this section, I investigated the effect of coagulant species on emission of gaseous pollutants especially for sulfur oxide (SO_x) generation. I set 4 typical case studies of coagulant usage based on the wastewater treatment flow. In case study 1 the usage of FeSO₄ and Al₂(SO₄)₃ were the same with the original model of textile sludge which is used

in clarification process A and clarification process B, respectively. Whilst in case study 2 the coagulant FeCl_3 was substituted for FeSO_4 on clarification A. However the coagulant used in clarification process 2 was still the same. Bidhendi et al. (2006) reported that although the optimum pH condition was a little different the optimum doses of FeCl_3 and FeSO_4 for color and COD removal, thus dose of FeCl_3 for simulation was set at the same with FeSO_4 . In case study 3, I changed the coagulant used on clarification B from $\text{Al}_2(\text{SO}_4)_3$ to FeCl_3 without changing the coagulant used on clarification A; the coagulant in clarification A for case 3 was FeSO_4 . According to the research conducting by Merzouk et al. (2011), the required dose of FeCl_3 is three times higher than $\text{Al}_2(\text{SO}_4)_3$ for color removal treatment. So the dose of FeCl_3 was set at three times higher than $\text{Al}_2(\text{SO}_4)_3$ in Case 3. Compare with case study 1, the coagulants for both clarification process were replaced by FeCl_3 in case study 4. The textile sludge model for each case study was summarized on the Table 3.7.

Table 3.7 Modeled textile sludge with difference coagulant species

Component	Composition (%)			
	Case study 1	Case study 2	Case study 3	Case study 4
Water content	60.039	60.039	59.796	59.796
Combustible matter	34.162	34.162	34.024	34.024
C	18.029	18.029	17.956	17.956
H	3.229	3.229	3.215	3.215
O	7.937	7.937	7.905	7.905
N	4.291	4.291	4.273	4.273
Volatile S	0.458	0.458	0.457	0.457
Volatile Cl	0.219	0.219	0.218	0.218
Ash content	5.799	5.799	6.180	6.180
SiO ₂	0.333	0.333	0.331	0.331
Al ₂ O ₃	0.175	0.175	0.174	0.174
Fe ₂ O ₃	0.060	0.060	0.060	0.060
CaO	0.244	0.244	0.243	0.243
Na ₂ O	0.178	0.178	0.177	0.177
K ₂ O	0.392	0.392	0.390	0.390
P ₂ O ₅	1.300	1.300	1.294	1.294
SO ₃	0.007	0.007	0.007	0.007
Cu	0.050	0.050	0.050	0.050
Zn	0.028	0.028	0.028	0.028
Pb	0.002	0.002	0.002	0.002
Sodium chloride (NaCl)	1.458	1.458	1.452	1.452
Sodium carbonate (Na ₂ CO ₃)	0.891	0.891	0.888	0.888
Coagulant (FeSO ₄)	0.235	-	0.234	-
Coagulant (FeCl ₃)	-	0.235	-	0.234
Lime (CaO)	0.001	0.001	0.001	0.001
Coagulant (Al ₂ (SO ₄) ₃)	0.203	0.203	-	-
Coagulant (FeCl ₃)	-	-	0.607	0.607

3.3 Simulation Procedure with MALT

The thermodynamic database of Material-oriented Little Thermodynamic (MALT) calculation was established firstly in 1986 by Japan Society of Calorimeter and Thermal

Analysis with the purpose to define the chemical behavior based on the chemical thermodynamic data (Yokokawa et. al., 1994). It was addressed for industrial application. After developing and improvement, the database of MALT stores about 4,932 compounds in gaseous, liquid, crystal and amorphous form (Yokokawa et. al., 1994). The gas simulation involved 16 elements consist of carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulfur (S), chlorine (Cl), phosphorus (P), silicon (Si), aluminum (Al), calcium (Ca), sodium (Na), iron (Fe), potassium (K), lead (Pb), copper (Cu) and zinc (Zn), and there were found around 765 chemical compounds in the gaseous and condensed form. The air ratio (λ) was set at 1.25 with 2.702 kg-N₂/kg and 0.821 kg-O₂/kg. The temperature of combustion chamber was controlled from 500 to 1100 °C.

3.4 Result and Discussion

3.4.1 *Thermodynamic equilibrium of textile sludge combustion*

The variation of partial pressure of textile sludge combustion as the function of temperature from 500 to 1100 °C are shown in Figure 3.2 Sulfur oxide (SO_x) in the form of sulfur dioxide (SO₂) sharply increased with increasing till 800 °C then become slightly increase to higher temperature. On the contrary sulfur trioxide (SO₃) started to decrease over 800 °C of combustion temperature. In accordance with literature, the generation of SO₃ was more preferred at lower temperature while the generation of SO₂ was preferred at higher temperature (Baukal, 2004). The generation of nitrous oxide (NO_x) in the form of NO is more sharply increased with increasing temperature than in the form of NO₂. The premier NO_x formation on the emission at higher combustion temperature is in the form of NO then rapidly reacts with oxygen to form NO₂ (Baukal, 2004). Thus, the generation of NO_x at high temperature is called thermal NO_x, which exponentially increases with the increasing of combustion temperature (Baukal, 2004). The partial pressure for the other gases was a plateau with the increasing temperature, except hydrogen chloride (HCl) gas,

which slightly decreased with increasing temperature over 900 °C.

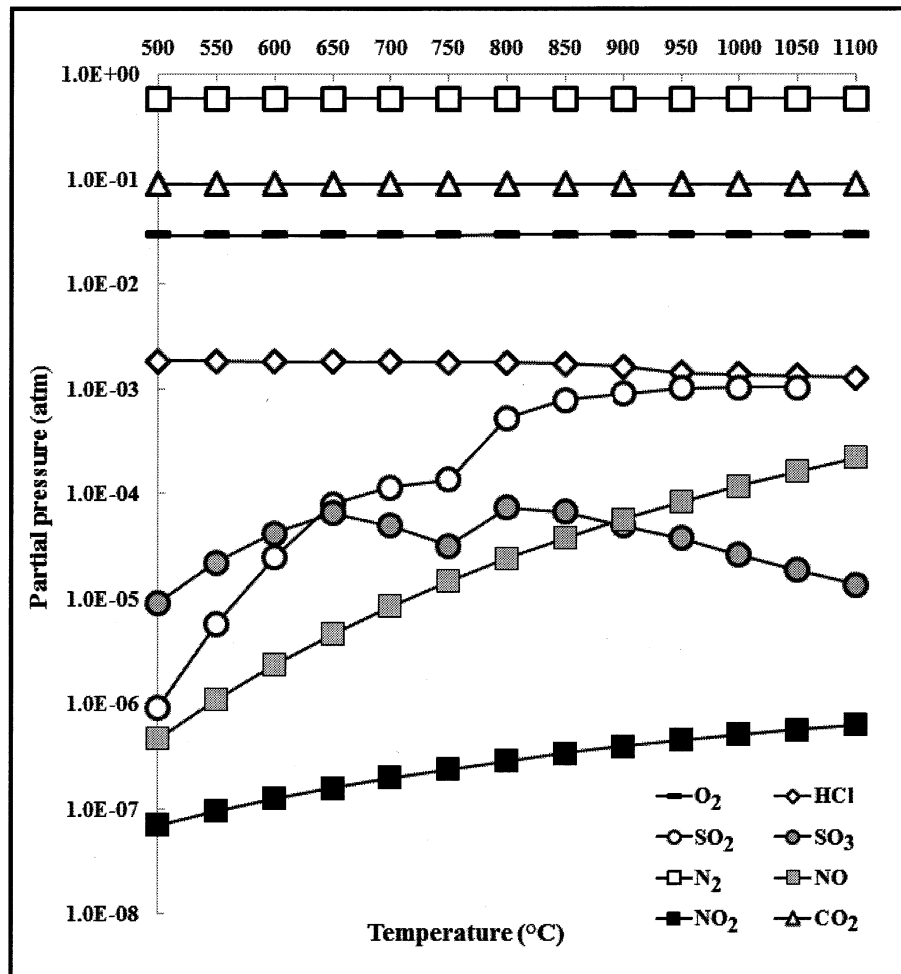


Figure 3.2 Partial pressure of textile sludge combustion

3.4.2 Typical gas emission

The gas emission based on its concentration as the result of textile sludge combustion is shown in Table 3.8. The generation of SO_x especially in the form of SO₂ must be concerned when the combustion temperature was performed at higher than 750 °C. It was noted that SO₂ concentration at 800 °C was 750.99 ppm that was over the standard emission regulation of 305.63 ppm in Indonesia (Keputusan menteri negara lingkungan hidup, 1995). The SO_x generation are predicted from the sulfur compounds on wastewater component, including contained in dyes and from coagulant used in clarification process. In the further necessary treatment the removal of SO₂ may be carried out through wet-type

limestone desulfurization process while in case of SO₃ removal a wet-type electrostatic precipitator process was more efficient (Kikuchi, 2001). On the contrary the concentration of NO_x (NO + NO₂) was still accepted by the Indonesian regulation (standard of NO₂ is 531.52 ppm) even at higher combustion temperature. Table 8 also mentioned that the concentration of carbon monoxide (CO) was very low even at higher combustion temperature. Generally the generation of CO is due to the incomplete combustion of carbon compounds when the lack of sufficient oxygen, insufficient temperature for whole reaction of CO and deficient time to complete the combustion (Baukal, 20041). However due to infinite combustion time of MALT, carbon compounds are completely burned till the depletion of oxygen which means oxidizing of carbon compounds reached complete combustion to form carbon dioxide (CO₂). It was thought to be the reason why the lower concentration of CO and higher concentration of CO₂ resulted by MALT simulation.

Table 3.8 Emission from textile sludge combustion as the function of temperature

Flue gas/ Temp (°C)	Concentration						
	500	550	600	650	700	750	
N ₂	82.83%	82.83%	82.83%	82.81%	82.81%	82.81%	
O ₂	4.15 ppm	4.15 ppm	4.15 ppm	4.15 ppm	4.16 ppm	4.16 ppm	
CO	0.00 ppm	0.00 ppm	0.00 ppm	0.00 ppm	0.00 ppm	0.00 ppm	
CO ₂	12.75%	12.75%	12.75%	12.75%	12.75%	12.75%	
NO	0.67 ppm	1.57 ppm	3.35 ppm	6.57 ppm	12.04 ppm	20.78 ppm	
NO ₂	0.10 ppm	0.14 ppm	0.18 ppm	0.23 ppm	0.28 ppm	0.34 ppm	
SO ₂	1.32 ppm	8.09 ppm	34.95 ppm	112.53 ppm	163.76 ppm	192.08 ppm	
SO ₃	13.01 ppm	31.47 ppm	59.81 ppm	92.74 ppm	70.13 ppm	45.62 ppm	
HCl	2614.50 ppm	2,616.80 ppm	2,593.91 ppm	2,561.20 ppm	2,556.16 ppm	2,547.76 ppm	
H ₂ O	29.36%	29.36%	29.36%	29.36%	29.36%	29.35%	
Flue gas/ Temp (°C)	Concentration						
	800	850	900	950	1000	1050	1100
N ₂	82.73%	82.68%	82.66%	82.64%	82.64%	82.63%	82.63%
O ₂	4.18 ppm	4.20 ppm	4.21 ppm	4.21 ppm	4.21 ppm	4.21 ppm	4.20 ppm
CO	0.00 ppm	0.00 ppm	0.01 ppm	0.02 ppm	0.06 ppm	0.17 ppm	0.44 ppm
CO ₂	12.74%	12.73%	12.73%	12.73%	12.73%	12.73%	12.73%
NO	34.18 ppm	53.77 ppm	81.28 ppm	118.78 ppm	168.37 ppm	232.41 ppm	313.33 ppm
NO ₂	0.41 ppm	0.48 ppm	0.56 ppm	0.64 ppm	0.73 ppm	0.81 ppm	0.91 ppm
SO ₂	750.99 ppm	1,111.02 ppm	1,280.59 ppm	1,438.96 ppm	1,455.62 ppm	1,466.41 ppm	1,473.66 ppm
SO ₃	104.92 ppm	95.81 ppm	70.98 ppm	53.20 ppm	37.06 ppm	26.46 ppm	19.33 ppm
HCl	2,530.01 ppm	2,474.74 ppm	2,307.77 ppm	2,008.97 ppm	1,971.14 ppm	1,911.37 ppm	1,821.00 ppm
H ₂ O	29.34%	29.32%	29.32%	29.32%	29.32%	29.33%	29.33%

3.4.3 Influence of coagulant species for SO_x and other gases generation

The influence of coagulant species for SO_x generation is shown on Figure 3.3. The concentration of SO_x for all case studies slightly increased until the combustion temperature of 750 °C then sharply increased and reached a plateau over 950 °C. The concentration of SO_x in the case study 4 was lower than other case studies, and the case study 1 was highest. If compared with case study 1, case study 4 was able to reduce around 18% of SO_x at 850 °C and 19% reduction was achieved over 950 °C of combustion temperature. This research indicated that coagulant species gave an influence for SO_x generation even though SO_x generation was still higher at high combustion temperature. In clarification A and B of case study 1, the sulfur content were coming from $FeSO_4$ and $Al_2(SO_4)_3$ of coagulant, otherwise there was no sulfur element in the form of $FeCl_3$ in case study 4. Accordingly sulfur content on coagulant belong to the sludge was thought to influence the SO_x production.

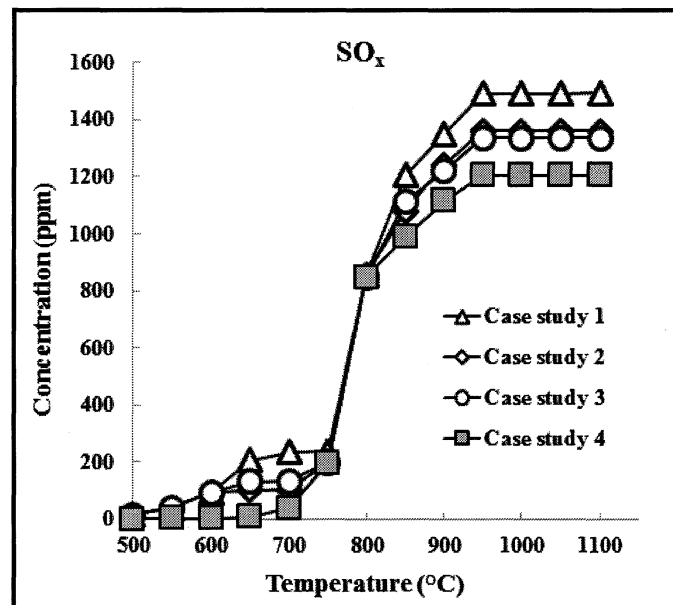


Figure 3.3 SO_x generation with different type of coagulant

The distribution ratio of sulfur element on Figure 3.4 shows the transformation of sulfur on the various molecule formations. The SO_x concentration was relatively low below 750 °C of combustion temperature. The sulfur element was dominated on K_2SO_4 and

Na_2SO_4 in the condensed form. The generation of SO_x on gaseous phase especially in the form of SO_2 started to be dominant when the combustion was performed not lesser than 800°C .

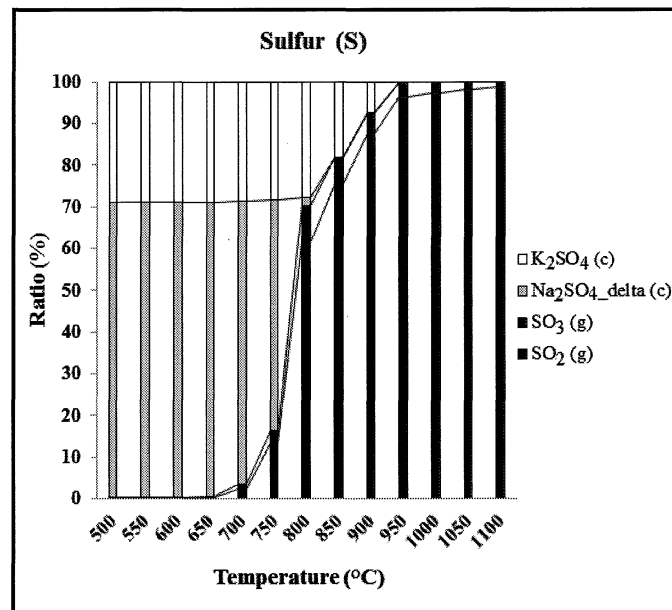


Figure 3.4 Distribution of sulfur element as the function of temperature

The change of coagulant type from FeSO_4 and $\text{Al}_2(\text{SO}_4)_3$ to FeCl_3 did not influence NO_x generation for all case studies as shown on Figure 3.5 NO_x concentration was almost the same in all case studies due to no change in the nitrogen content on coagulant.

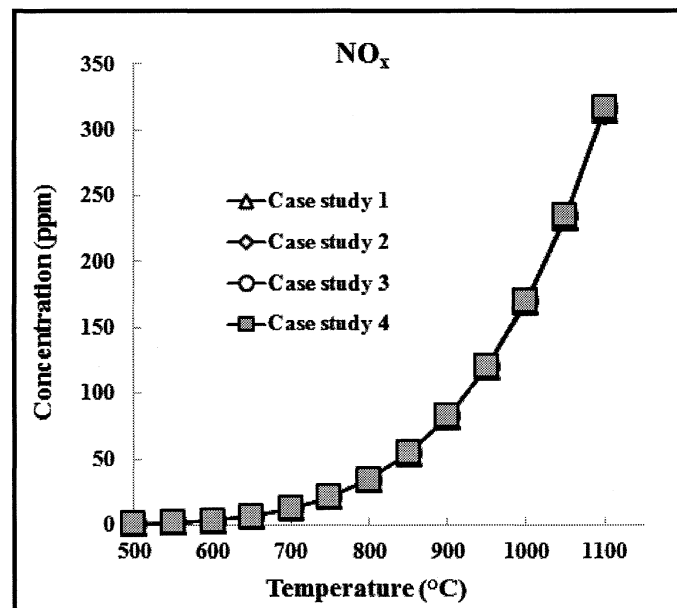


Figure 3.5 NO_x generation with temperature as the effect of coagulant type

Basically for all case studies the HCl concentration was relatively stable at the combustion temperature of 800 °C or less then slightly decrease with the increase in the combustion temperature as shown in Figure 3.6.

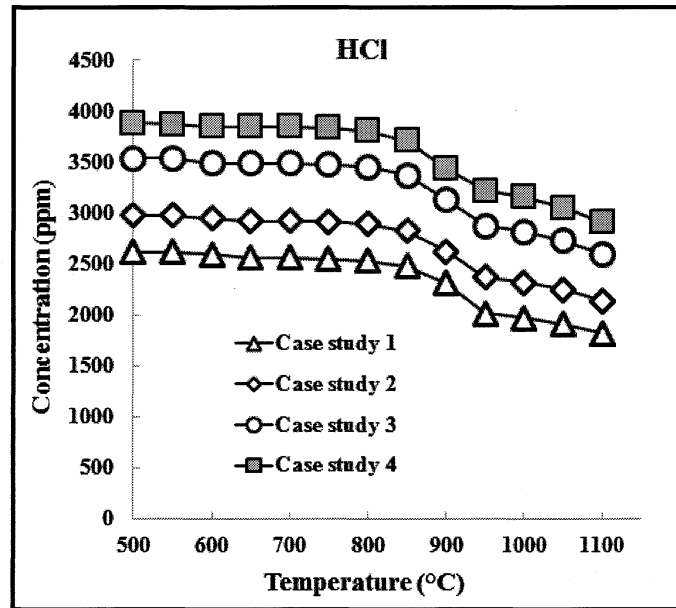


Figure 3.6 HCl generation with temperature as the effect of coagulant type

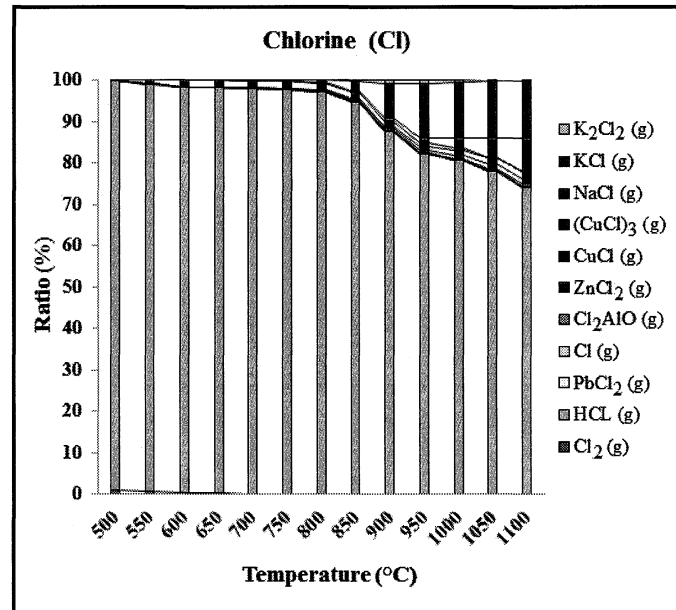


Figure 3.7 Distribution of chlorine element as the function of temperature

The comparison between case study 4 and case study 1 shows that the substitute of coagulant from FeSO_4 and $\text{Al}_2(\text{SO}_4)_3$ to FeCl_3 resulted in an increase of the concentration of HCl gas. The change of sulfur compounds to the chlorine compound of coagulant was

thought to cause the increase in HCl concentration on case study 4. While refer to the distribution ratio of chlorine compounds on Figure 3.7, HCl were a premier compound at the low combustion temperature. However, HCl concentration slightly decreased with increasing the combustion temperature since the chlorine formed other compounds such as KCl, NaCl, and CuCl. On the other hand lower combustion temperature may reduce the generation of CuCl gas. CuCl is known as a catalyst for dioxin formation in case of fly ash (Fujimori, 2007).

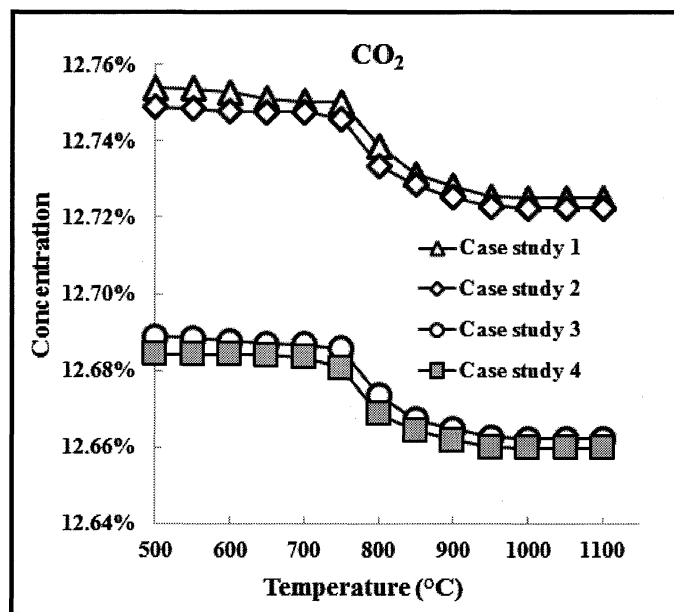


Figure 3.8 CO₂ generation with temperature as the effect of coagulant type

The change of coagulant species from FeSO₄ and Al₂(SO₄)₃ to FeCl₃ was no significant influence on the CO₂ emission. It can be seen on the Figure 3.8 by the comparison of CO₂ concentration between case study 4 and case study 1.

3.5 Conclusion

The typical gas emissions from textile sludge combustion were simulated by the Material-Oriented Little Thermodynamic (MALT) calculation. The result reported that various types of gas with different concentrations were released as flue gas of the textile sludge combustion. The generation of SO_x, especially on the form of SO₂ must be

concerned when the combustion treatment was performed at higher than 750 °C. Otherwise the generation of NO_x was still acceptable by Indonesian regulation for gas emission even though the combustion was performed at higher temperature (more than 1000 °C). The influence of coagulant species for gas emission was also investigated in this study. The simulation demonstrated that the replacing coagulant species in clarification process A and B from FeSO₄ and Al₂(SO₄)₃ to FeCl₃ was able to reduce 18% of SO_x generation at the combustion temperature of 850 °C and 19% at the temperature not less than 950 °C. The use of sulfur free coagulant could reduce the SO_x generation though its concentration was still high at higher temperature (more than 750 °C). On the contrary the substitution of coagulant FeCl₃ for FeSO₄ and Al₂(SO₄)₃ enhanced the generation of HCl gas. Replacing the sulfur content to chlorine content on coagulant type was thought to cause the increase in HCl emission on case study 4. On the other hand there was no significant effect on NO_x and CO₂ gas as the replacement of coagulant species in this study due to no change in nitrogen and carbon content belong to the coagulant species.

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Chapter IV

Recycle of Textile Sludge Ash for Brick Manufacturing

4.1 Introduction

The problem of the textile sludge is caused not only by the large amount of quantity but also by the toxic and hazardous material as a residue from various chemical agents used during textile processing and textile wastewater treatment. Landfilling is a common process for sludge disposal. However this process may cause ground water pollution due to landfill leachate and has a possibility of limiting land application (Turovskiy and Mathai, 2006). Various recycling technologies have been applied to converting sludge into valuable products, like for cement (Taruya et al., 2002; Cyr et al., 2007; Garces et al., 2008) for fertilizer (Milne and Graveland, 1972; Cox, 1995; Franz, 2008), for brick production (Weng et al., 2003; Tay, 1987; Baskar et al., 2006), for material adsorbents (Jeyaseelan and Qing, 1996; Martin et al., 2004; Xu et al., 2005) and other applications as a method solving sludge disposal problems. In this research, brick production for construction material can be one of alternative option for sludge utilization, because a thermal process involving brick production from sludge is possible to immobilize toxic and hazardous material by heat treatment (Turovskiy and Mathai, 2006). In brick production, compressive strength and water absorption play an important role in determining the quality of brick. Previous researches mentioned that the textile sludge could replace clay (Baskar et al., 2006; Balasubramanian et al., 2006; Patel and Pandey, 2009; Raghunathan et al., 2010). Baskar et al. (2006) investigated that 6–9% of textile sludge addition could reach the minimum Indian Standard of compressive strength and standard minimum of water absorption could be achieved by 16–17% of sludge addition. In addition Balasubramanian et al. (2006) found that 10% of sludge addition in brick production can be acceptable by minimum standard compressive strength and 30% is still

acceptable for water absorption. According to the previous researches the possibility of textile sludge as a material substitute for clay in the brick formation was informed. However, the increasing of sludge addition deteriorated the quality of brick, especially lowered the compressive strength. Considering the recent status of sludge utilization as bricks, increasing the sludge addition rate with a great quality standard in the brick production became a new challenge in this study.

Waste glass, a material with non-biodegradable characteristic has been reported for many applications in the recycling field. Coirinaldesi et al. (2005) showed that the addition of glass powder on the sample specimen could improve the durability of concrete products. It was reported that the combination of limestone powder waste and waste glass for a new brick material met the quality of compressive strength, flexural strength, water absorption and other parameters (Turgut, 2008). In addition European Waste Catalogue noted that the glass obtained from bottle waste is categorized as a non-hazardous waste (Furlani et al., 2010). Therefore, this research discussed the effect of waste glass addition in the sludge-clay brick formation with hopes to get a better quality of brick product in accordance to the industrial standard parameters.

4.2 Material

Textile sludge was received from one of textile industries in Wakayama Prefecture. The characteristic of sludge was explained in the previous Chapter II. Clay was obtained from one of local brick companies in Aichi Prefecture (Figure 4.1a). Bottle waste was used as a raw material for waste glass (Figure 4.1b). Table 4.1 shows the chemical composition of raw material which was analyzed with Energy dispersive X-Ray spectrometer type EDX-800HS (Shimadzu, Japan).

Table 4.1 Chemical composition of raw material for brick production (dried based)

Composition	Sludge ash (%)	Clay (%)	Waste glass (%)
SiO ₂	10.3 ± 0.2	49.1	72.7
TiO ₂	3.1 ± 0.1	1.2	0.4
Al ₂ O ₃	44.2 ± 1.0	15.7	5.9
Fe ₂ O ₃	10.7 ± 0.2	8.0	0.7
MnO	0.1 ± 0.0	0.1	0.1
MgO	1.9 ± 0.0	2.0	1.9
CaO	2.8 ± 0.0	2.7	12.3
Na ₂ O	12.8 ± 0.3	10.1	13.9
K ₂ O	1.0 ± 0.0	2.9	1.6
P ₂ O ₅	2.9 ± 0.1	1.5	0.7
SO ₃	3.0 ± 0.5	0.4	0.4

Notes: the sample was triplicated (average data was obtained)

In case of textile sludge it was received two times from the company, so the average of chemical composition was provided on Table 4.1. EDX analysis shows the primary component of clay were SiO₂ (49.1%) and Al₂O₃ (15.7%), whereas waste glass was dominated by SiO₂ (72.7%). Sludge ash compositions were mostly occupied by Al₂O₃ (44.6%), SiO₂ (11.0%) and Fe₂O₃ (10.2%). According to the Lin (2006), Al₂O₃, SiO₂ and Fe₂O₃, which show on the chemical composition of sludge, were preferable to sintering application.

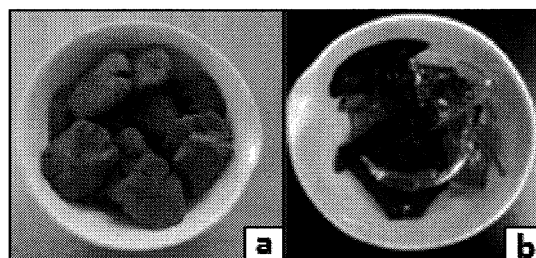


Figure 4.1 Clay (a) and bottle waste as waste glass (b)

4.3 Method

4.3.1 The formation of brick

The production process of textile sludge-based brick followed the flowchart on Figure 4.2.

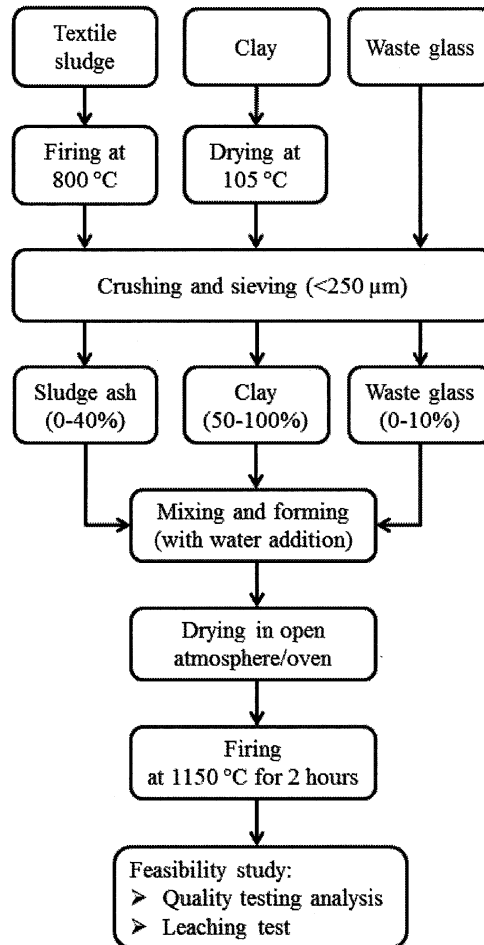


Figure 4.2 Production process flowchart of textile sludge-based brick

Firstly, textile sludge was fired at 800 °C for 2 hours to eliminate various organic matters and to get the ash content with a muffle furnace FO410 model (Yamato, Japan). Clay was dried at 105 °C overnight to remove water content with dryer FP-300 model (Toyo Seisakusho, Ltd. Japan). Sludge ash, dried clay and waste glass were crushed with a cyclone mill 1033-300A model (Yoshida Seisakusho, Japan) and sieved to homogenize their size below 250 μm with a testing sieve (IIDA Manufacturing Co., Ltd, Japan), respectively. Brick formations were carried out with various addition rate of sludge from

0–40% while the waste glass was added in 5% or 10%, respectively. The raw materials were mixed with the various composition ratios with adding adequate amount of water to facilitate the mixing formation. The mixture was formed with dimension of $\phi 3 \text{ cm} \times 3 \text{ cm}$ of height with a tube-shaped mold. Green brick then pressed with a hydraulic jack type MH-15 (Masada Seisakusho, Japan) at 1 MPa to form a solid composition. Depend on the weather the brick specimen was dried at open atmosphere for one day or at dryer FP-300 model (Toyo Seisakusho, Ltd. Japan) for overnight. Firing process was then conducted at 1150 °C in muffle furnace FO410 model (Yamato, Japan) for 2 hours. The firing process was actually carried out by 2 hours for increasing temperature, 2 hours for firing process and 2 hours for decreasing temperature. This time program was conducted to avoid cracking on brick body during the heating and cooling process.

4.3.2 Compressive strength procedure

In order to investigate the quality of brick, quality tests were carried out for compressive strength and water absorption based on Japan Industrial Standard *JIS R1250 for common brick*. Compressive strength evaluates the material capacity to resist the axial force per unit area. The specimen will break when the axial force reaches the maximum strength (White, 1999). Compressive strength is one of important parameters in building and construction material, especially for the product strength to withstand the load. According to the *JIS R1250 for common brick*, the quality of brick is divided into three categories in compressive strength: first quality when brick has compressive strength $>30 \text{ N/mm}^2$, second quality is $30\text{--}20 \text{ N/mm}^2$ and third quality is $20\text{--}15 \text{ N/mm}^2$. The compressive strength test was carried out with a 250 kN universal testing machine (AG-250kNX, Shimadzu, Japan) with the load axially at uniform rate was $1 \text{ N}/(\text{mm}^2 \cdot \text{s})$. Compressive strength can be measured when the product reaches the maximum load at failure. It calculated by following equation (4-1). The samples of compressive strength test

were obtained for not less than three times.

$$\text{Compressive strength (N/mm}^2\text{)} = \frac{\text{Maximum load at failure (N)}}{\text{Area dimension (mm}^2\text{)}} \quad (4-1)$$

In addition surface morphology of brick product was also observed to investigate the effect of sludge and waste glass addition on brick formation. Electron probe micro analyzer (EPMA) type JXA-8900JR (JEOL, Japan) under the acceleration voltage of 15 kV, 25 mS of dwell time, probe current of 5.0×10^{-8} mA and 500 times of magnification was run to observe the surface structure and elemental formation. Moreover digital imaging was also conducted at 200 times of magnification with a digital microscope VH-5000 (Keyence, Japan).

4.3.3 Water absorption procedure

Water absorption is an essential factor on brick product related to the durability (Baskar et al., 2006). According to *JIS R1250 for common brick*, first quality of brick has water absorption below 10%, for second and third quality brick must has water absorption lesser than 13% and 15%. Water absorption was measured following the procedure: firstly, the brick product was dried in drying oven at 105 °C for more than 24 hours and cooled down to a room temperature, then the brick is weighed to get m_1 . The dried brick product was immersed in water for more than 24 hours and then wiped before weighed to get m_2 . The percentage of water absorption can be obtained by following the equation (4-2). Water absorption test was carried out for three times replication

$$\text{Water absorption (\%)} = \frac{m_2 - m_1}{m_1} \times 100\% \quad (4-2)$$

4.3.4 Shrinkage and weight loss procedure

The change of brick dimension as the result of firing process was determined by

percentage of shrinkage. Volume of brick before and after firing was compared and measured with vernier calipers. On the other hand to investigate the effect of firing process on the change of weight, weight loss was measured by comparing weight of brick before and after firing process. Related to the weight loss, Thermo-gravimetric differential thermal analysis (TG-DTA) was conducted to investigate the raw material (sludge ash, clay, glass) that gives the effect on weight change of brick product. TG-DTA was performed with TG-DTA 2000 SA (Bruker AXS, Japan). A couple Al_2O_3 crucible contained 10 ± 0.3 mg of dried samples (raw material) and $\alpha\text{-Al}_2\text{O}_3$ as a standard were prepared then heated until the temperature reached $1250\text{ }^\circ\text{C}$ at the heating rate of $10\text{ }^\circ\text{C}/\text{min}$ with air flowing. Percentage of shrinkage and weight loss analysis was conducted for three times replication.

4.3.5 Heavy metal leaching procedure

Heavy metal leaching test was conducted to investigate heavy metal content on raw material of brick and brick product based on *Japan Leaching test No 46*. The procedure of the leaching test as follows: The sample was crushed and sieved to obtain the sample size lesser than 2 mm. The sample was diluted by distilled water on 1/10 of solid/liquid ratio. The pH of solution was checked with a pH meter (Horiba, Japan) then adjusted by addition of 1M of hydrochloric acid (HCl) to 5.8-6.3. The solution was shaken at 250 rpm for 6 hours with a shaking machine of Recipro shaker SR-2w (Taitec, Japan) followed by standing for 30 minutes. The sample then was centrifuged at 3000 rpm for 20 minutes with a centrifugation machine (Beckman Coulter, USA) before doing filtration with $0.45\text{ }\mu\text{m}$ of filter paper (Whatman, Japan). The content of chromium (Cr), manganese (Mn), nickel (Ni), copper (Cu), zinc (Zn) and lead (Pb) was examined from the filtrate sample with an inductively coupled plasma (ICP) spectrometer type Optima 5300 DV (Perkin Elmer, Japan). However in case of chromium content, the result from this procedure was Total-Chromium. Hexavalent chromium (Cr(VI)) on the sample was

observed based on *Japan Industrial Standard for hexavalent chromium investigation*. The procedure was as follows: A solution containing filtered sample of leaching test was stirred at 400 rpm of 80 °C with a magnetic stirrer type Rexim RSH-1D (As One, Japan). During this process, 1 mL of ammonium iron (III) sulphate ($\text{Fe}(\text{NH}_4)(\text{SO}_4)_2$) was added into the solution. The pH was checked with a pH meter (Horiba, Japan) then adjusted to 8-9 by addition of ammonia (NH_3). The sample was filtered with a filter paper (5A, Whatman, Japan). The used filter paper containing the solid residue from the filtration was washed with ammonium nitrate (NH_4NO_3), which was heated at 80 °C before used for washing. The chromium content on filtered sample was then analyzed with the ICP spectrometer. From this procedure, the chromium obtained by ICP analysis was hexavalent chromium. All samples were triplicate for the leaching test procedure.

4.4 Result and Discussion

4.4.1 Compressive strength test

Compressive strength data for textile sludge-based brick with or without glass addition are provided on Figure 4.3. The compressive strength of brick without glass addition was relatively stable with the increase of sludge addition. In addition statistical analysis of t-test with a hypothesis of significant difference also mentioned that the substitution of sludge for clay had no significant influence on the compressive strength (p value > 0.05). Actually, the area dimension of brick became smaller with increasing the amount of sludge due to the shrinkage effect of sludge as indicated by the percentage shrinkage on Figure 4.9. Compressive strength value was influenced by the maximum strength and area dimension of brick as noted on the equation (4-1). The high maximum strength and small area dimension will achieve high compressive strength. Therefore, the stable compressive strength with the addition of sludge on Figure 4.3 would be reached by the decrease in the area dimension. Furthermore in order to improve the compressive

strength, waste glass was added into the textile sludge-clay composition. Figure 4.3 showed that the addition of waste glass intensified the compressive strength.

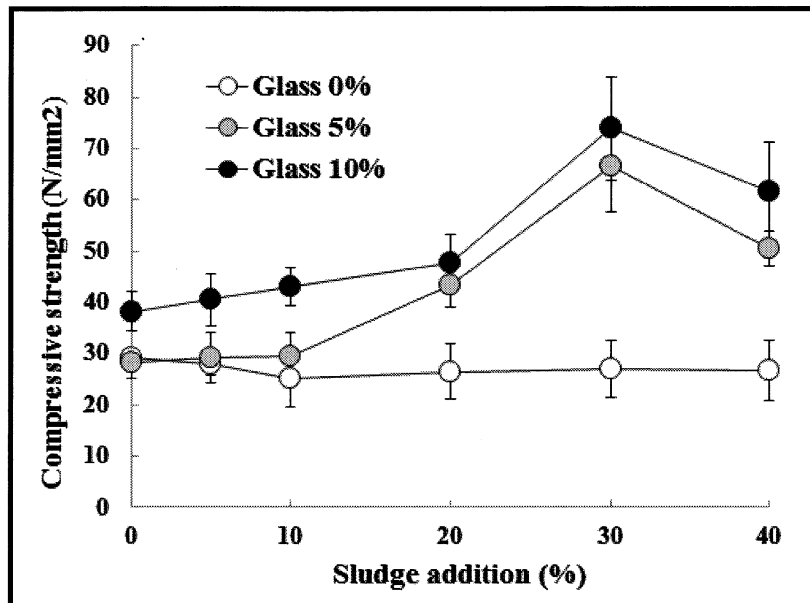


Figure 4.3 Compressive strength test result of brick product, the error bar means the unbiased standard deviation of replicated sample

The addition of waste glass started from 5% with insignificant result of compressive strength until the sludge addition reached 20% (p value > 0.05). While when the waste glass was added at 10% the significance result was already achieved by the brick made from clay 90%-glass 10% compare with brick from 100% clay (p value < 0.05). Figure 4.3 informed that the maximum compressive strength was reached when the sludge and glass were added at 30% and 10%, respectively. The result regarding the effect of waste glass on clay brick was also reported by Chidiac and Frederico (2007); Dondi et al. (2005) who showed that the addition of waste glass improved the quality of compressive strength on brick product. If I refer to the first grade standard of brick, the addition of sludge at 40% with 5% or 10% glass addition was actually still acceptable. However the forming process of brick with over the 30% of sludge addition was difficult to be done due to the nature of low adhesiveness of sludge. Moreover the increasing sludge addition also increases the shrinkage effect. If the more sludge addition is considered as a substitute for

sludge disposal, the sludge addition until 40% is acceptable, though the compressive strength of brick will be deteriorated. The surface image of brick was observed with the EPMA on Figure 4.4 to 4.6 and the digital microscope on Figure 4-7. The EPMA analysis not only shows the mapping image but also provides elemental formation of the section analyzed. The brick with clay 100%, brick with clay 60%, sludge 40% and brick with clay 50%, sludge 40% and glass 10% can be compared using Figure 4.4, 4.5 and 4.6. Compositional image (CP) section on Figure 4.4 shows that the brick with 100% clay has a smooth structure on the surface. The surface of brick seemed to lead to rough when the sludge was added (Figure 4.5). The waste glass addition improves the surface structure of brick become smoother as shown on the CP part of Figure 4.6. The substitution from clay into sludge reduces the concentration of silica (Si) on the brick as shown on the Figure 4.4 and Figure 4.5 on the Si mapping section. Silica is well known as a main component of clay brick. On the contrary, the aluminum (Al) concentrations increase with addition of sludge as shown on the Al mapping image of Figure 4.4 and Figure 4.5. It was also noted by the chemical composition analysis with EDX on the Table 1 that the main component of sludge is Al_2O_3 . The addition of waste glass improved Si concentration on the brick, which is shown on the silica section on Figure 4.6 compare with Figure 4.5. Moreover waste glass addition also increased the concentration of sodium (Na) and calcium (Ca) on the brick. On the other hand, Figure 4-5 on the oxygen (O) map shows that there were many pores created by the addition of sludge in comparison with Figure 4.4 of brick with clay 100%. The similar effect was reported by Wiebusch and Seyfied (1997), who mentioned that the addition of sewage sludge ash enhanced pore formation and water adsorption, and reduced in the specific gravity. The pores formation was thought to deteriorate the quality of brick. However the pores tend to reduce when the waste glass was added as shown on the oxygen map on Figure 4.6. To investigate the effect of waste glass addition relating to the pores on the surface morphology, digital imaging of surface area of brick was conducted. Digital

imaging of brick with clay 100%, brick with clay 60%, sludge 40% and brick with clay 50%, sludge 40% and glass 10% are shown on Figure 4.7a, 4.7b and 4.7c. In comparison with Figure 4.7b, the melted glass could clog up the pores as shown in Figure 4.7c. This research revealed when the melted glass covered the pores it was affecting to increase the compressive strength.

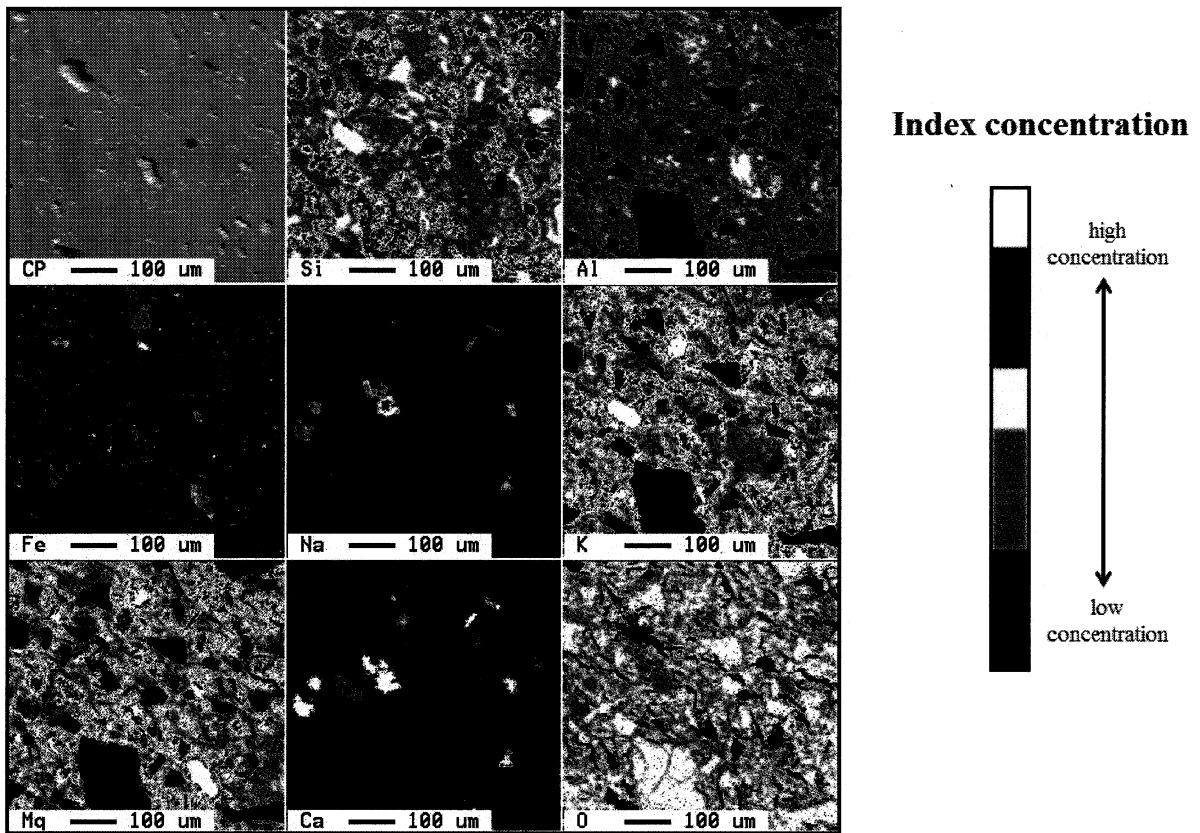


Figure 4.4 EPMA of brick with composition of clay 100%

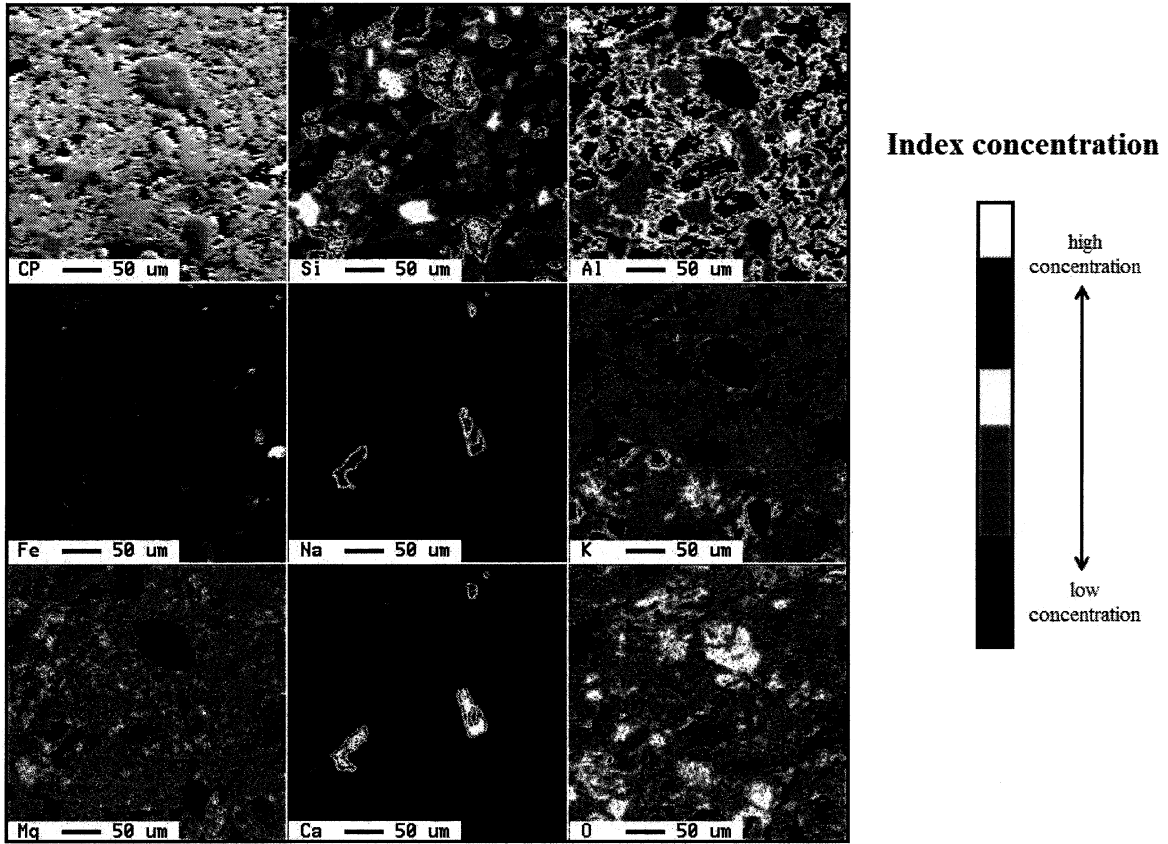


Figure 4.5 EPMA of brick with composition of clay 60% and sludge 40%

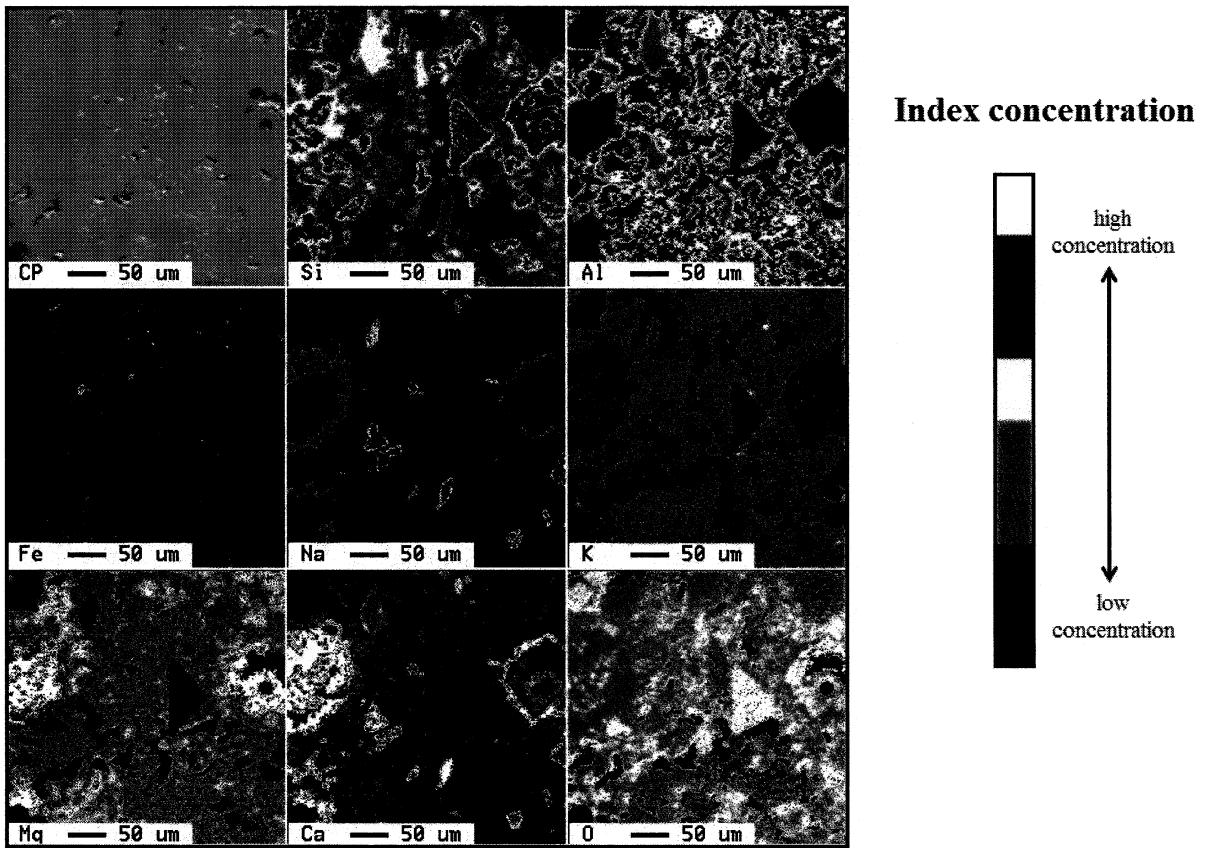


Figure 4.6 EPMA of brick with composition of clay 50%, sludge 40%, and glass 10%

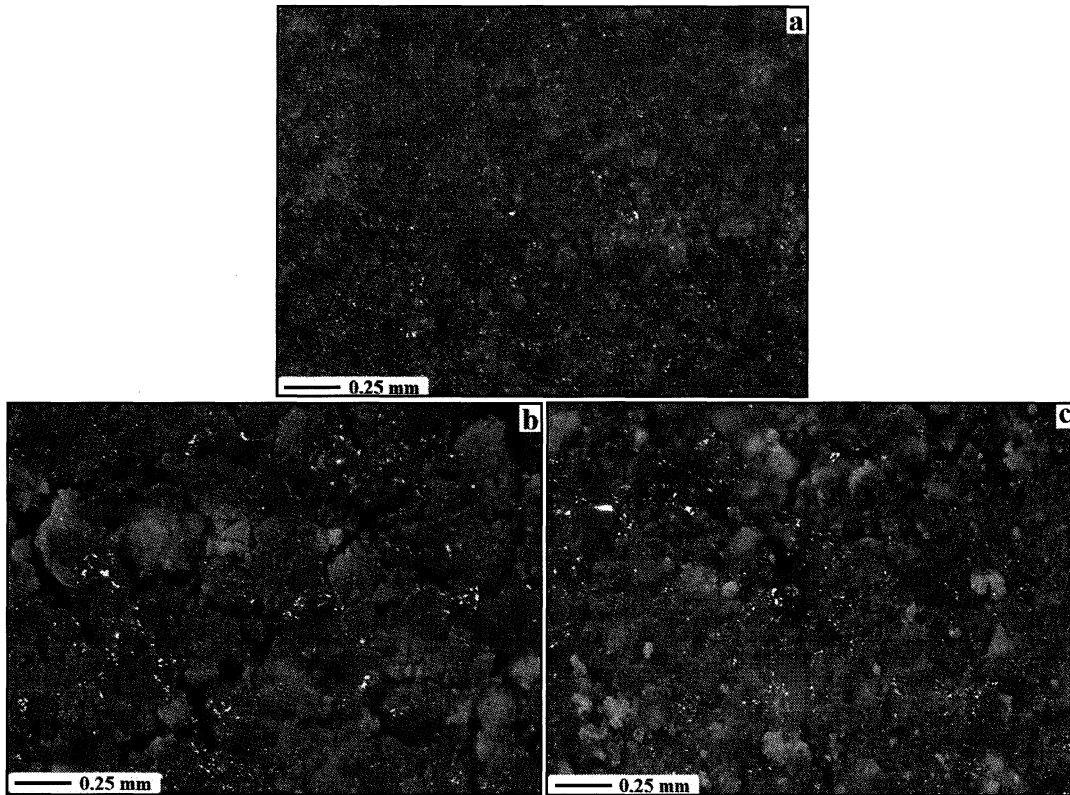


Figure 4.7 Digital imaging of brick with composition of clay 100% (a), clay 60%, sludge 40% (b) and clay 50%, sludge 40%, glass 10% (c)

4.4.2 Water absorption test

Figure 4.8 shows that the water absorption of brick without glass addition increased with enhancing sludge addition. Moreover sludge addition over 5% made the brick product out of first grade standard. Furthermore with more than 20% of sludge made the brick out of the standard limit quality. The EPMA analysis mentions that the sludge addition enhanced porosity in the brick (Figure 4.5). Cusido and Cremades (2012) on their research of clay brick produced with sewage sludge reported that sintering process at high temperature affected the porosity on the microstructure of brick due to the destroying of organic matter. The pores formation made brick more easily to absorb the water. Digital imaging on Figure 4.7c shows with the addition of glass the pores could be clog up by the melted glass. It decreased the water absorption to brick as shown on Figure 4.8. Chidiac and Frederico (2007) also supported that the addition of waste glass countered the porosity problem on the fired clay by fixing the pore distribution.

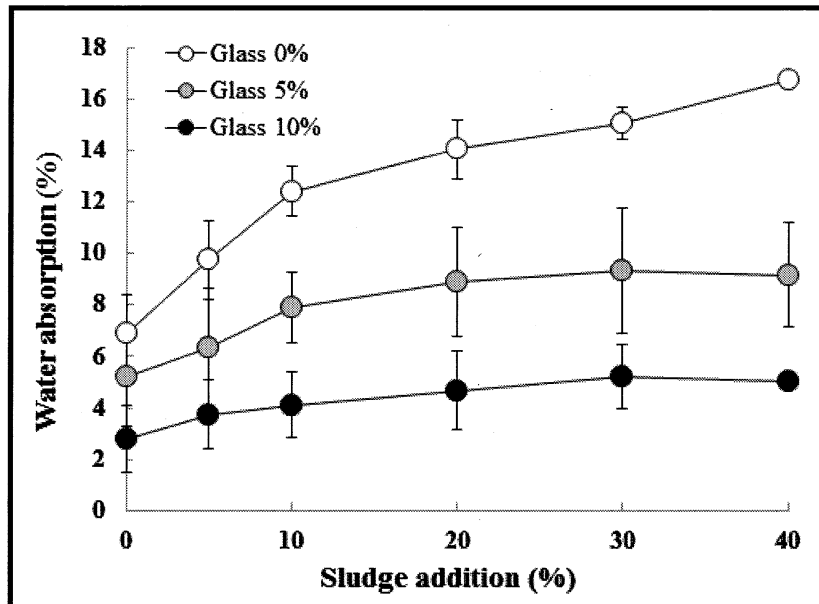


Figure 4.8 Water absorption test result of brick product, the error bar means the unbiased standard deviation of replicated sample

4.4.3 Percentage of shrinkage and weight loss

Figure 4.9 shows that the percentage of shrinkage increased with increasing the sludge addition. This means that the brick product becomes smaller than the raw brick before firing. The addition of glass also enhanced the shrinkage as the result of melting process. Figure 4.10 shows that the addition of sludge was no effect on weight of brick product. But glass addition slightly decreased the weight loss. This means brick with glass addition will little bit heavier than without glass addition. It also supported by TG-DTA analysis on Figure 4.11, which shows that the weight loss of glass has lesser than clay and sludge during firing process.

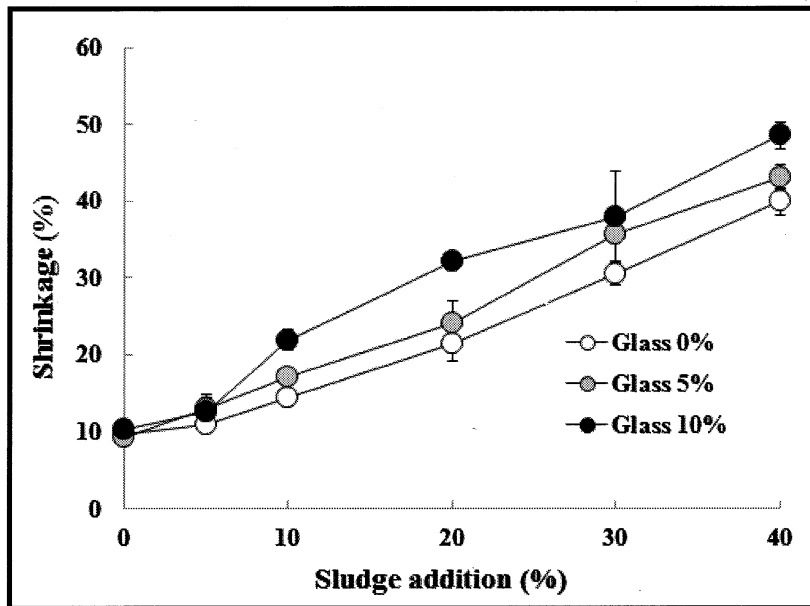


Figure 4.9 Percentage of shrinkage of brick product, the error bar means the unbiased standard deviation of replicated sample

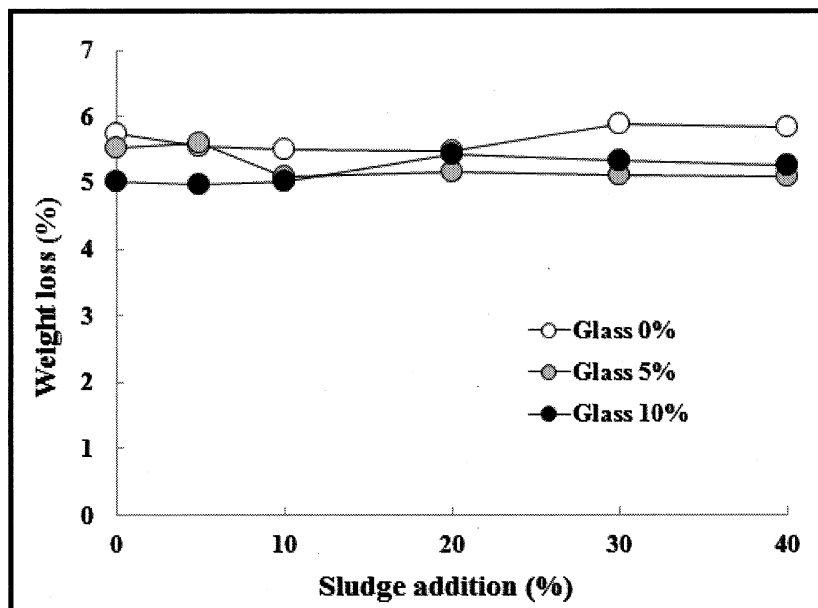


Figure 4.10 Percentage of weight loss of brick product

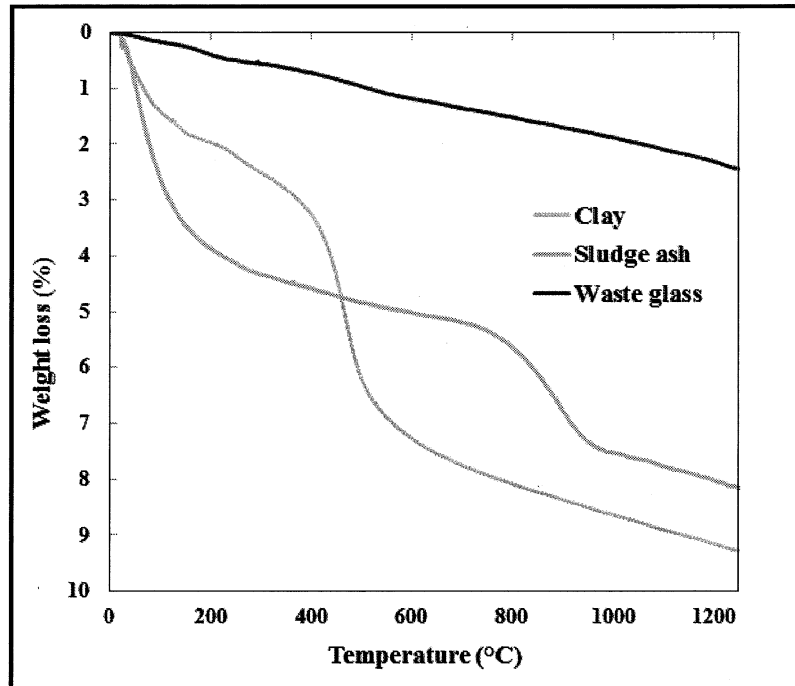


Figure 4.11 TG-DTA of raw material for brick production

4.4.4 Heavy metal leaching test

The impression of sludge coming from hazardous material like heavy metal has restrained the utilization of recycle products using sludge for common applications. In this section, I investigated the heavy metal leaching characteristic of textile sludge-based brick. Table 4.2 shows the leaching behavior of raw material for brick production especially on clay and sludge. Leaching test resulted in the lead (Pb) concentration of leachate from the dried sludge exceeded the standard limit of Japan Leaching Test No. 46 ($0.089 \text{ mg/L} > 0.010 \text{ mg/L}$). Although the dried sludge was not be used for brick production, it indicated that the sludge contained heavy metals. In addition the concentration of hexavalent chromium (Cr(VI)) of leachate from sludge ash was over the standard regulation ($0.089 \text{ mg/L} > 0.050 \text{ mg/L}$). The high concentration of some heavy metals may be induced by the usage of various chemical agents on textile chemicals and/or auxiliary chemicals during textile processing. Moreover they might derive from chemicals used during the wastewater treatment process. Anyway, it should be noted that the textile sludge can be categorized as

a hazardous material and need more concern for disposal. Leaching test was also conducted for brick product as noted on Table 4.3. It shows that most of heavy metals were not detected in leachates from the brick products. Although a few heavy metals were detected in the leachates, their concentrations still meet the standard regulation. As aforementioned, the recycling process involving heat treatment has an advantageous by immobilizing the toxic and hazardous compounds. Lin (2005) reported on his research regarding the effect of SiO_2 and Al_2O_3 on the hydration of MSWI fly ash that during firing process, some heavy metal compounds were volatilized and the rest were immobilized by fixation into matrices including inert silicates. Accordingly, heat treatment contributes to less leachability of heavy metals from the brick product. As the Si-O matrix formation conducted to stabilize non-volatile heavy metals (Lin, 2005), the addition of waste glass, which was abundant in silicates compound, improved the leaching behavior of textile sludge-based brick. This research in cooperation with Wiesbuch and Seyfried (1997) demonstrated that the substitution of sludge for part of clay for brick production was acceptable from an environmental point of view in leachability of heavy metals.

Table 4.2 Leaching behaviour of raw material

Element	Concentration (mg/L)		
	Clay (dried base at 105 °C)	Sludge (dried base at 105 °C)	Sludge ash (800 °C)
Total-Cr	n.d.	n.d.	0.157
Cr(VI)	n.d.	n.d.	0.089
Mn	0.060	0.308	n.d.
Ni	n.d.	0.034	n.d.
Cu	n.d.	0.010	n.d.
Zn	n.d.	n.d.	n.d.
Pb	n.d.	0.089	0.006

Notes: *n.d.* refers to no detection which means the concentration of element less than 0.001 mg/L. The sample was triplicated (average data was obtained)

Table 4.3 Leaching behaviour of brick product with various compositions ratio

Element	Concentration (mg/L)			
	Clay 100%	Clay 60%, sludge 40%, glass 0%	Clay 55%, sludge 40%, glass 5%	Clay 50%, sludge 40%, glass 10%
Total-Cr	n.d.	n.d.	0.012	n.d.
Cr(VI)	n.d.	n.d.	n.d.	n.d.
Mn	0.012	0.004	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.
Cu	n.d.	0.001	n.d.	n.d.
Zn	n.d.	n.d.	n.d.	n.d.
Pb	n.d.	n.d.	n.d.	n.d.

Notes: n.d. refers to no detection which means the concentration of element less than 0.001 mg/L. The sample was triplicated (average data was obtained)

4.5 Conclusion

The utilization of textile sludge ash as a raw material for clay substitute on brick manufacturing was evaluated in this research. The addition of sludge over 5% could not satisfy the water adsorption criteria for the first grade of brick, and the brick with sludge addition over 20% was below the third grade criteria. The addition of waste glass to the sludge-clay formation for brick production could improve the compressing strength and water absorption parameters of the textile sludge-based brick. The brick made from textile sludge ash: 30%, clay: 60% and waste glass: 10% reached the highest compressive strength and the water adsorption of 5%, which satisfied the first grade standard of brick product according to the *JIS R1250 for common brick*. Surface morphology analysis showed that the waste glass melted during firing process clogged up pores on the brick. It was thought to affect the improvement of the water adsorption and the compressive strength. Leaching tests were also conducted to check the leachability of heavy metal compounds from brick product. The result informed that there was no environmental restriction for the use of the brick product using textile sludge ash as a raw material. Thus, the combined use of textile sludge and waste glass into brick production were satisfied both technical and

environmental aspects. Moreover it will contribute to solve the problem of textile sludge disposal.

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Chapter V

Feasibility Study of the Application of Textile Sludge-based Adsorbent for a Real Wastewater

5.1 Introduction

Adsorption techniques receive much attention for color removal in recent years. Activated carbon is well known as a good adsorbent due to its high adsorption capacity. However the high price of activated carbon becomes a problem for the cost efficiency. Various adsorbents produced from low cost materials were investigated as potential adsorbents for color removal such as: zeolite (Armagan et al., 2004), sepiolite (Alkan et al., 2004), chitosan (Yoshida et al., 1993) sunflower stalks (Sun and Xu, 1997), recycled alum sludge (Chu, 2001), etc. In the case of adsorption researches for color removal, the adsorption tests were often performed in a pure aqueous solution instead of a real wastewater. The feasibility study in real wastewater is necessary for the practical application, because coexistence of other contaminants may interfere the adsorption performance. The adsorbent may adsorb other contaminants except a target one. In adsorption applications, there are many factors affecting the treatment performance, which are not only the nature of adsorbent like surface area, ion exchange capacity, pH of adsorbent, etc. but also the nature of its solution itself, like pH of solution, the degree of particle target, etc (Worch, 2012). In my previous research the textile sludge was successfully converted into a potential adsorbent through carbonization process (Chapter II). The carbonization at 600 °C was selected as the optimum temperature to create larger specific surface area of 138.9 m²/g on carbonized sludge compared with other carbonization temperatures. The research demonstrated that carbonized sludge had 60.30 mg/g of adsorption capacity for methylene blue removal. Based on previous research I tried to investigate the removal capacity of carbonized sludge at 600 °C in a real

wastewater in this chapter. Calculating the necessary adsorbent dose for complete removal of color from the wastewater was evaluated in this research. In addition, since the daily adsorbent production rate from sludge depended on the daily sludge production rate from the system itself, the feasibility of the application of carbonized sludge to the real wastewater was demonstrated by comparing the sludge production rate and the necessary adsorbent production rate.

5.2 Material

Textile sludge was received from one of textile industries in Wakayama Prefecture, Japan. The sludge was carbonized at 600 °C for 2 hour with a Muffle Furnace F0410 (Yamato, Japan). Carbonized sludge at 600 °C was selected as an adsorbent. Wastewater was obtained from a restaurant at Ryukoku University, Japan. While a methylene blue powder was received from Nacalai Tesque, Japan. Then methylene blue was diluted with deionized water to get the exact concentration for the research. The raw wastewater consists of 500 mL of the restaurant wastewater and 100 mL of methylene blue with 500 mg/L. In addition, 400 mL of activated sludge was added for the activated sludge process. Consequently, the initial concentration of methylene blue was 43.8 mg/L in the wastewater and 9.7 mg/L in the mixed liquor of the wastewater and the activated sludge.

5.3 Experimental Method

Firstly 500 mL of the restaurant wastewater and 100 mL of the methylene blue solution was poured into a 1L of plastic container. The pH, color, and chemical oxygen demand (COD) of the mixture were then checked. The color was analyzed with UV-2550 UV-Visible Spectrophotometer (Shimadzu, Japan) at the peak wavelength (λ_{\max}) of 665 nm after centrifugation at 2900 rpm for 15 minutes. The pH of wastewater was measured with a pH meter (Horiba, Japan). Chemical oxygen demand (COD) was analyzed based on closed reflux, colorimetric method (Standard method for examine wastewater: 5220 D,

1998). Both Total-COD and Dissolved-COD were determined. The experimental procedure as follows (Figure 5.1): Firstly the activated sludge treatment was applied on this system by adding 400 mL of activated sludge on the raw wastewater as shown on Figure 5.2. Aeration was conducted for 8 hours followed with sedimentation for 3 hours.

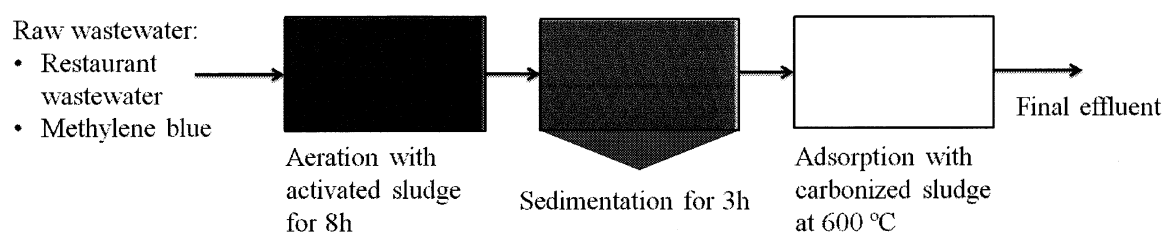


Figure 5.1 Scheme of activated sludge and adsorption treatment combination

Sedimentation was carried out to separate suspended solids in the solution after the activated sludge treatment. After the sedimentation process, the supernatant solution was separated from activated sludge. The pH, color and COD then measured again with the same procedure as explained before. In order to remove the residual color of the solution, the adsorption treatment was applied.

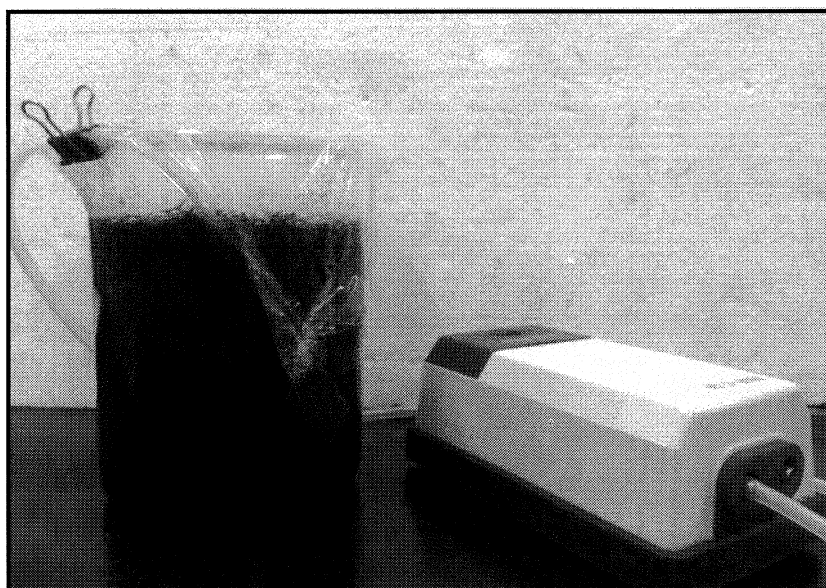


Figure 5.2 Experimental set up for aeration experiment

A series of 300 mL of conical flasks containing various amounts of adsorbent and 100 mL of the solution were shaken with a bio-shaking machine, series TB-9R-3F (Takasaki

Scientific Instrument Corp., Japan) at 150 rpm at 25 °C for 1280 minutes (21 hours 20 minutes). The adsorbent input was set at 0.005 to 0.04 g. Finally the pH, color and COD were measured for the final effluent.

5.4 Result and Discussion

5.4.1 Activated sludge and adsorption performances for COD and color removal

The mixed liquor had 657 mg/L of T-COD with 43.8 mg/L of methylene blue concentration and pH of 6.5. As shown on the Table 5.1 that activated sludge system has 85.6 % removal efficiency for T-COD and 89.2% for D-COD. The COD after aeration treatment was 94.8 mg/L for T-COD and 60.4 mg/L for D-COD. Activated sludge treatment also has 76.6% of color removal efficiency.

Table 5.1 Wastewater treatment performance of activated sludge and adsorption treatment

Activated sludge system				Adsorption system				
T-COD removal (%)	D-COD removal (%)	Color removal (%)	pH after	Adsorbent mass (g)	D-COD removal (%)	D-COD Final effluent (mg/L)	Color removal (%)	pH after
85.6	89.2	76.6	8.0	0.005	29.2	42.8	53.0	8.1
				0.01	32.8	40.6	79.0	8.0
				0.02	40.3	36.1	100	8.0
				0.03	40.8	35.7	100	8.2
				0.04	49.5	30.5	100	8.1

Notes: the sample was triplicated (average data was obtained)

In order to reach the complete removal of color, adsorption treatment was applied on this system. Table 5.1 noted the performance ability of adsorption treatment with the function of adsorbent mass. Actually, when refer to the calibration curve of methylene blue 0.02 g of adsorbent was estimated to remove 100% of color. However judging from the visual images (Figure 5.3), a little color still remained on the solution after 0.02 g of adsorption

treatment. Therefore, in order to consider the safety factor, 0.03 g of adsorbent was chosen as the suitable amount of adsorbent on this system, which was equivalent to the adsorbent dose of 0.3 g/L-wastewater. In this condition, the D-COD removal efficiency reached 40.3%. In order to investigate the inhibition factor by other contaminants in wastewater, the comparison between predicted-residual concentration and observed-residual concentration of effluent was carried out. Based on the research on the Chapter II, carbonized sludge at 600 °C has a maximum capacity (q_{\max}) of 60.30 mg/g with Langmuir capacity factor (K_L) was 0.851 L/g for removal synthetic wastewater of methylene blue. The predicted-residual concentration can be estimated by substituting the equation (2-1) to equation (2-2), so the equation (5-1) will be obtained as follows:

$$\frac{(ObsC_o - ObsC_e)V}{m} = \frac{q_{\max} \times K_L \times PredC_e}{1 + K_L \times PredC_e} \quad (5-1)$$

Where: $ObsC_o$ is observed-initial concentration (mg/L), $ObsC_e$ is the observed-residual concentration (mg/L) and $PredC_e$ is the predicted-residual concentration (mg/L). The $ObsC_o$ was known has 2.28 mg/L after aeration treatment and become initial dye concentration for adsorption treatment. Actually when the residual concentration was completely removed (0 mg/L), the adsorption capacity becomes difficult to determined, so in this case I only compared the adsorbent mass of 0.01 and 0.005 g. When $PredC_e$ equal/higher than $ObsC_e$ means that there were no inhibitions during color removal treatment by other contaminants, on the contrary when $PredC_e$ lower than $ObsC_e$, it means other contaminants interferer the adsorbent for uptaking dye molecule into surface of adsorbent. As shown on the Table 5.2 $PredC_e$ was lower than $ObsC_e$ at 0.005 g of adsorbent while $PredC_e$ was higher than $ObsC_e$ at 0.03 g. Due to the adsorbent dose at 0.03 g was preferable for completely color removal, I deduced that the carbonized sludge at 600 °C was almost no inhibition during methylene blue adsorption in the real wastewater.

Table 5.2 Comparison between predicted-residual concentration and observed-residual concentration

Adsorbent mass (g)	PredC _e (mg/L)	ObsC _e (mg/L)
0.005	0.79	1.07
0.01	0.50	0.48
0.02	0.27	0
0.03	0.17	0
0.04	0.12	0

Notes: the sample was triplicated (average data was obtained)

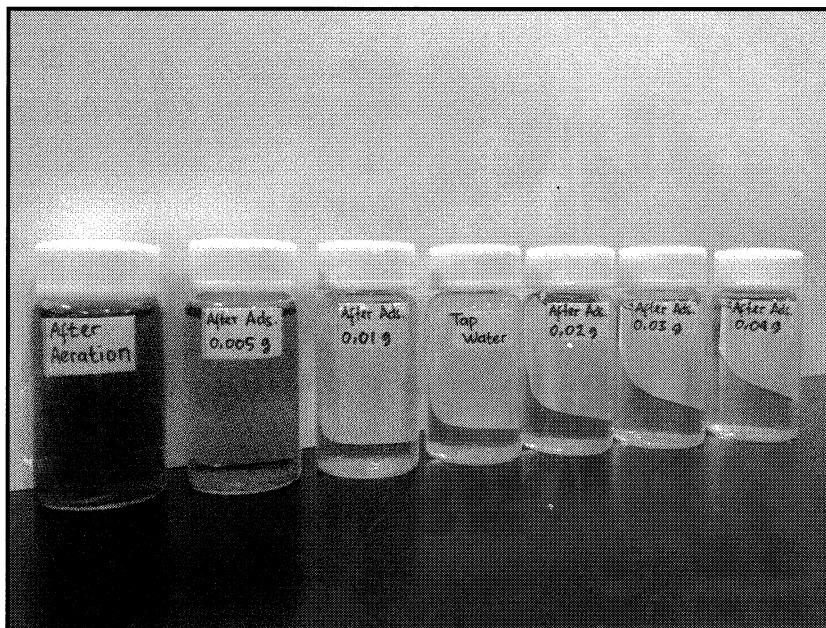


Figure 5.3 Adsorption treatments in the real wastewater with a function of adsorbent mass

5.4.2 The adsorbent mass balance for color removal

In reference to the half reaction (McCarty, 1975) the sludge production from activated sludge can be estimated by following equation (3-5) on Chapter III as below.

$$SP = \left[(COD_{input} \times IL) - (COD_{output} \times EL) \right] \times \frac{113}{224}$$

The sludge production depends on the COD in the wastewater and the COD removal efficiency in the activated sludge process. As noted on the previous section about the COD and the removal efficiency, the sludge production on this system can be estimated to be

283.5 mg sludge/ L-wastewater. When the sludge was utilized into adsorbent, the final production of adsorbent was reached around 115.2 mg due to 59.4% of weight loss during the carbonization at 600 °C. The solid/ liquid ratio of adsorbent mass to the volume of wastewater for complete color removal was 0.3 g/L. Therefore, according to the mass balance on this system the utilization of textile sludge-based adsorbent via carbonization process was able to supply 38.4% of the required amount of adsorbent.

5.4.3 Countermeasure for lack of adsorbent

5.4.3.1 The regeneration of carbonized sludge at 600 °C

There are two optional choices to handle the lack of adsorbent in this system. The one of them was regeneration of carbonized sludge at 600 °C. In this section, I investigate the ability of carbonized sludge regenerated at 600 °C. The carbonized sludge dried at 105 °C overnight after adsorption was carbonized again with the same procedure of carbonization as mentioned on the Chapter 2. The regeneration had a function to remove color on the adsorbent by a thermal process. The carbonized sludge was then tested for color removal.

Table 5.3 Regeneration performance of carbonized sludge at 600 °C

Number of Replication	Weight loss (%)	Capacity loss (%)
1	12.3	15.2
2	14.7	15
3	14.3	11.1
Average	13.8	13.8

As noted on the Table 5.3 that 13.8% of adsorbent weight and 13.8 % of adsorption capacity will loss during re-carbonization. However the result indicated that the regeneration of carbonized sludge was applicable.

5.4.3.2 Introduction of synthetic talc

Another way of optional choices to solve the lack of adsorbent is an introduction of additional adsorbent. Here, I introduced synthetic talc as an additional adsorbent, which was prepared in Laboratory of Kurosaki Hakudo Industries Co., Ltd., Japan. Synthetic talc is a synthesized material from silica and magnesium hydroxide (Komaki et al., 2006). Clay material such as synthetic talc was introduced as a low cost material compared with activated carbon and showed great ability for color removal treatment. Rahman et al. (2013) demonstrated that the synthetic talc has the highest adsorption capacity than various clay adsorbent like: zeolite, sepiolite, kaolin, and bentonite for removal of Reactive Procion dyes. In this section, the adsorption capacity of synthetic talc was investigated for methylene blue removal. As shown on the Figure 5.4 the methylene blue adsorption onto the synthetic talc reached an equilibrium after the contact time of 640 minutes. The contact time of synthetic talc for the equilibrium was shorter than that of the carbonized sludge. In addition the maximum capacity of synthetic talc showed four times higher than that of carbonized sludge, which was 255.34 mg/g for methylene blue removal.

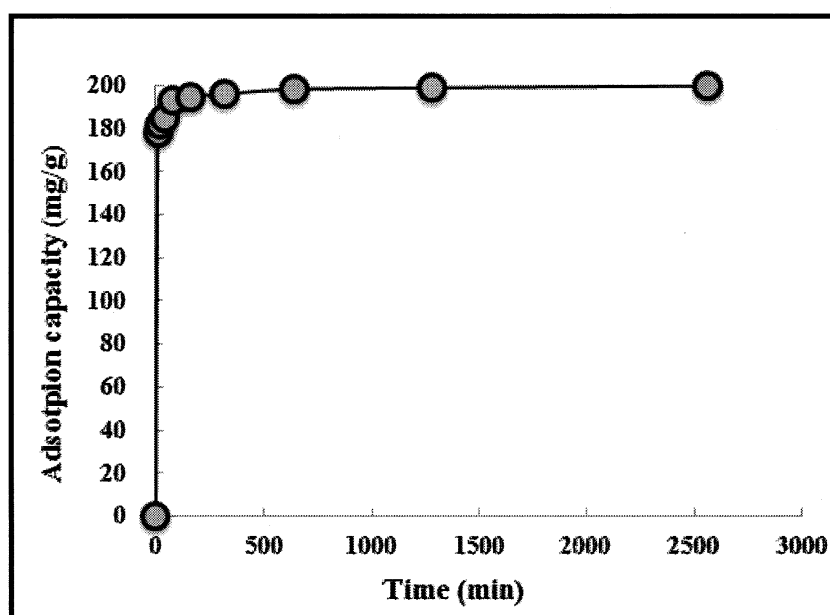


Figure 5.4 Adsorption equilibrium of synthetic talc with a function of time

In addition to methylene blue treatment, I have investigated the regeneration ability of synthetic talc after color removal of Reactive Yellow 138:1. As shown on Figure 5.5 the removal efficiency of Reactive Yellow 138:1 using the synthetic talc regenerated at 400 °C of heating treatment or higher reached the same capacity as that using new synthetic talc. Moreover the weight loss during regeneration was below 10%. Thus, it was indicated that synthetic talc may be repeatedly available for the color removal application.

Table 5.4 Adsorption isotherm parameter of synthetic talc

Freundlich Isotherm Parameter			Langmuir Isotherm Parameter		
1/n	K_f (mg/g)(L/mg) ^{1/n}	R ²	q_{max} (mg/g)	K_L (L/mg)	R ²
0.05 ± 0.004	201.52 ± 3.88	0.97	255.34 ± 3.90	1.09 ± 0.35	1.00

Notes: the sample was triplicated (average data was obtained)

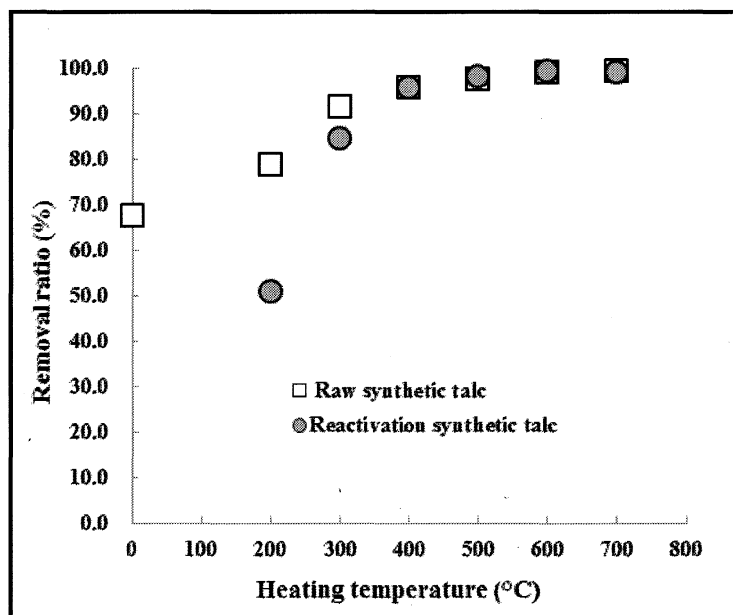


Figure 5.5 Regeneration ability of synthetic talc for the treatment of Reactive Yellow 138:1

5.5 Conclusion

The feasibility study of the application of textile sludge-based adsorbent in a real wastewater was discussed in this research. The carbonized sludge was able to remove methylene blue from the real wastewater with almost no inhibition by other contaminants.

The mass balance was also calculated according to the necessary adsorbent for complete color removal and the sludge production from the activated sludge system. The result indicated that the utilization of textile sludge-based adsorbent via carbonization process was able to supply 38.4% of the required adsorbent. In addition to counter the lack of adsorbent for complete color removal, the reuse of carbonized sludge was discussed and it was proved that the regeneration of carbonized sludge could be applicable, though 13.8% of adsorption capacity was lost during the regeneration process. An additional adsorbent called synthetic talc was tested to evaluate the adsorption performance of methylene blue for assisting the textile sludge-based adsorbent. Consequently, it showed a greater ability than the carbonized sludge; a faster adsorption time and four times higher of adsorption capacity than carbonized sludge. Moreover the adsorption capacity of synthetic talc regenerated at 400 °C or higher showed no deterioration compared with that of the virgin synthetic talc. Therefore, synthetic talc was thought to be a potential adsorbent compensating the lack of carbonized sludge.

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Chapter VI

Final Conclusion

6.1 Proposed Framework for the Treatment of Colored Wastewater and Textile Sludge

The whole research in this paper demonstrated a technical review of an appropriate treatment for colored wastewater and sludge disposal derived from textile industry activity. At the beginning, textile sludge was successfully converted into potential adsorbent for color removal treatment. Carbonization at 600 °C was suitable to produce the optimum surface area of carbonized sludge-based adsorbent (138.9 m²/g). In addition the ability for color removal was achieved by 60.30 mg/g of adsorption capacity for the removal of a cationic dye, methylene blue. On the other hand for anionic dye removal, lower carbonization temperature was more preferable especially at 400 °C.

The flue gas simulation analysis showed that the combustion temperature should be performed at lesser than 800 °C to minimize the SO_x emission. Moreover the coagulant species evidently influenced the SO_x generation. Using a free-sulfur compound of coagulant (replacing coagulant from FeSO₄ and Al₂(SO₄)₃ to FeCl₃) was able to reduce 18% of SO_x generation when the combustion temperature was set at 850 °C and 19% at the temperature not lesser than 950 °C.

The recycle of textile sludge ash into bricks can become an alternative method to final disposal of sludge. The brick composed of textile sludge ash 30%, clay 60% and 10% of waste glass reached the maximum compressive strength with only 5% of water absorption that satisfied the first grade of brick product based on Japan Industrial Standard *JIS R1250 for common brick*. Moreover, the toxicity characteristic leaching test showed that the heavy metal leachability was minimized due to heat treatment during brick

production. It means that the brick product is available to common purposes from the environmental point of view.

The feasibility study demonstrated that the textile sludge-based adsorbent via carbonization was able to remove color from the real wastewater with almost no inhibition observed. In addition the mass balance showed that the usability of textile sludge-based adsorbent could solve 38.4% of colored wastewater problem. The regeneration of carbonized sludge and synthetic talc may be promising as an additional adsorbent to reach the completely color removal treatment.

As the result of this research, I proposed a new concept to solve both the colored wastewater problem and the textile sludge disposal as shown in Figure 6.1.

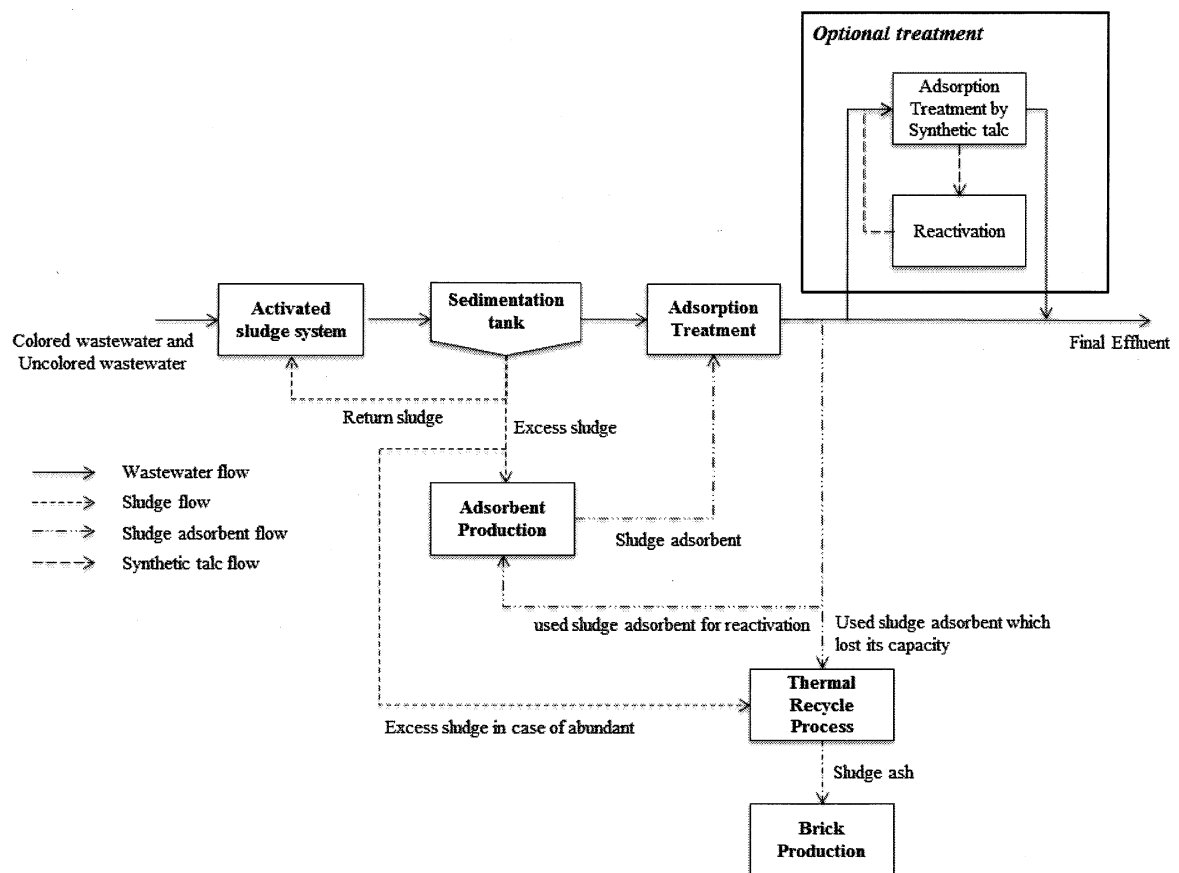


Figure 6.1 Integrated treatment systems of colored wastewater and textile sludge

This integrated treatment system suggests that the mixed wastewater (colored wastewater and uncolored wastewater) is supplied to the activated sludge system, which is a

pretreatment of the adsorption process for decolorization and produces excess sludge for the adsorption production. The adsorbent in adsorption process will be obtained from the excess sludge of activated sludge treatment through carbonization process. In a case of the shortage of the sludge, a carbonized sludge regeneration process may be possible to be introduced or/and the co-usage of another adsorbent called synthetic talc can be recommended. The stable adsorption capacity of synthetic talc under the repeated reactivation will be a suitable option to handle remaining colored wastewater and to achieve the complete removal for the final effluent. The final sludge disposal will be handled by recycling textile sludge ash for brick manufacturing. In summary there are some benefits in the new concept of integrated treatment system as follows:

1. Substituting the adsorption process for the clarification process will reduce the coagulation sludge generation and will eliminate the cost of coagulants and flocculants.
2. The adsorbent material will be free because it comes from the excess sludge.
3. The utilization of textile sludge for the adsorbent production and the brick production will eliminate the disposal problem of sludge.

Thus, I propose a schematic integrated treatment system with hopes to solve environmental problem derived from textile industry in order to support cleaner production technologies.

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6.3 Acknowledgement

Praise is for Allah SWT – God the beneficent and the merciful for granting me countless blessing.

First and foremost, I would like to convey the deepest gratitude to my advisor, Professor Naoyuki KISHIMOTO. It has been an honor to be a member in his laboratory. Many valuable lessons were got during completing the doctoral degree under his guidance. His expertise in water quality system engineering improved my research skill and prepared me for the future challenge. I appreciate all his contribution of time, ideas and insightful discussion about the research.

I owe to deepest gratitude to Dr. Takeo URABE (Professor Emeritus of Ryukoku University) for creating a basic foundation of my research in solid waste management.

Personally, I am deeply thankful to the Dr. Shinji MIZUHARA for advice, discussion and teaching instrumental analysis, Mr. Teiji SATO from Kurosaki Hakudo. Co., Ltd., for synthetic talc sample and information, Hinode Sengyo Co., for textile sludge, Okamoto Renga for clay material, Industrial research center of Shiga Prefecture for compressive strength test, Ryukoku extension center for EPMA analysis, Ms. Yukie MIHARA for SEM analysis, Mr. Kazuki IKEDA for discussion on textile sludge-based activated carbon research, Indonesian textile research center for study literature and other companies/institutes for visiting research, valuable discussion and sample analysis. Moreover, I also thank to the members of Kishimoto laboratory for many helps and discussion in the area of water and wastewater treatment.

I would also like to offer my Thank you to Dr. Yoshiaki GOTO (Professor Emeritus of Ryukoku University) and his family for their support, valuable discussion and kind attention during studying in Ryukoku University.

In addition, I wish to express my gratitude to the MEXT: Ministry of Education, Culture, Sports, Science, and Technology, Japan and Ryukoku University for the financial support of scholarship in supporting my study.

Last but not least, I would like to thank to all of those whom supported me during finishing doctoral thesis and studying in Ryukoku University, Japan.