Cotton Dyeing wastewater characteristics and its treatment efficiency by using coconut shell carbon and limestone powder

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Abstract: Application of adsorption treatment for textile wastewater has been studied for years. However, there is very limited data available on the development of eco-friendly composite adsorbent derived from coconut shell activated carbon (CSAC) and limestone powder (LP) as the core materials and sea-weed algae as the core binder. An attempt was made to determine the effect of sequential treatment of individual adsorbent specifically for the removal of COD, color and Cu (II) from cotton dyeing wastewater. From single stage adsorption procedure, CSAC dosage of 8 g/L. was able to remove 49%, 45% and 31% of COD, colour and Cu (II), respectively. Meanwhile, 6 g/L, of LP was found optimum to remove more than 34% of the same parameters. The results also revealed that in order to obtain spherical bead of adsorbent, 1 to 3 % (w/v) of sea-weed algae was required. Furthermore, increasing the molarity of calcium crosslinks led to better beads formation in the ranges of 3 -5 mM.

Key words: Adsorbent; Coconut shell activated carbon; Composite; Limestone powder; Wastewater

1. Introduction

Textile industries are known as water intensive users at which, continuous increase in demands for textile products in domestic and export markets has been the reason for large volume of untreated wastewater (dos Santos et al., 2007). In general, every stage of textile production has its environmental impacts, from fiber production through manufacturing until finished goods. Textile wastewater generated from these processes includes a large variety of dyes and chemical additions (Al-Kdasi et al., 2004), whereby managing the wastewater is crucial to the manufacturers in order to comply with government legislation and environmental protection. Adsorption process is considered to be a superior option because of its convenience, ease of operation and simplicity of design which capable of removing heavy metals (Al-Ghouti et al., 2010), color (Syafalni et al., 2012), COD (Ahmad et al., 2012) and organic contents from synthetic and actual textile effluents (Ahmad et al., 2013).

Activated carbon is one of the oldest known adsorbent that is widely used in adsorption processes. It has a very porous structure with a large surface area (Bhatnagar and Sillanpää, 2010). Because of chemical and mechanical stability, high adsorption capacity and high degree of surface reactivity, activated carbon is an ideal adosrbent nominated over other adsorbents currently (Malik et al., 2007). Despite these advatanges, activated carbon suffers from high cost of production that encompasses from high energy requirement during activation to regeneration constraints (Foo and Hameed, 2010; Gupta, 2009). Besides, separation of activated carbon from treated wastewater using traditional separation methods including filtration and sedimentation may result in blocking the filters as well as loss of adsorbent.

Meanwhile, limestone based adsorbent also is widely used in water and wastewater treatment. For example, fluoride removal from groundwater sample was pre-treated with phosphoric acid prior adsorption process which increased its adsorption capacity (Gogoi et al., 2015). Also, due to excellent properties including high specific surface area and high dispersivity, vaterite $CaCO_3$ shows high selectivity for positively charge in the Congo red molecule (Chong et al., 2014). However, by prolonging adsoprtion process, limestone filter may cause structure disintegration and filters clogged up. This phenomenon would lead to precipitation that eventually increases pH of the water being treated. Moreover, single use of activated carbon and limestone in wastewater treatment is not cost-effective unless it is prepared to adsorb metals and organic parameters simultaneously. Therefore, a study to reduce adsorbent's surface deterioration is needed to address this limitation.

Composite adsorbent is mostly produced by mechanical mixing between minerals and carbon compunds. This type of adsorbent is characterized by specific properties, whereby their surfaces have a mosaic characteristic that can adsorb both organic and inorganic substances simulatenously (Leboda et al., 2006). Consequently, the idea of sea-weed algae containing activated carbon and limestone particles

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is considered as promising technique in dealing with recalcitrant pollutants removal. Having the hydrophobic and hydrophilic characteristics, the surface of the composite adsorbent can be tailored and therefore the surface charge of the composite could be neutralized or reversed and its surface may become hydrophobic to hydrophilic and vice versa.

In this first stage of work, coconut shell activated carbon and limestone powder was tested towards pollutants removal from cotton dyeing wastewater by batch studies. The removal trend for each of the parameters being studied was investigated by batch studies. The wastewater obtained was sourced from actual cotton dyeing wastewater to simulate the efficiency of COD, color and Cu (II) removal by composite adsorbent in batch studies. Rheological property of sea-weed algae and effects of Ca^{2+} ions were studied in order to produce a spherical bead composite.

2. Material and methods

2.1. Chemicals

All chemicals used in the study is listed in Table 1. The chemicals were used as received without further purification. Prior to conducting the experimental works, the material safety data sheet (MSDS) of all the chemicals were read and used based on supplier guidelines

2.2. Composite adsorbent preparation

The composite adsorbent preparation involved several physical and mechanical procedures which have been suggested by Annadurai et al. (2002). Slight modification was adopted in order to tolerate

different characteristics of CSAC and LP. First, known amount of freshly CSAC and LP powder was introduced into 500 mL beaker. A known volume of distilled water was then added and stirred with mechanical stirrer (Ika, Germany) for 15 minutes with 50 rpm speed. Next, the beaker was heated to 80 °C on a hot plate and sea-weed alage powder was slowly added into the beaker. This process was maintained for 15 minutes until a homogeneous condition between CSAC, LP and seaweed algae was obtained.

The mixture was then extruded from the pre-fabricated injector by controlling the opening of control valve. Finally, the ejected mixtures were immersed in $CaCl_2$ solution for 12 hours in order to achieve rounded and hardened beads. Schematic illustration of the experimental set-up is shown in Fig. 1.

3.1. Batch adsorption studies

In this study, the treatability of CSAC and LP was individually tested via batch studies. One factor at time (OFAT) approach is one of commonly used technique involving factors or causes, one at a time instead of all simultaneously. In addition, the number of experiments is limited; whereby the primary aim is to achieve improvement in the system that is being investigated, which could be realized with minimum error. In this study, the removal of CSAC and LP towards the removal of COD, color and Cu (II) were tested via OFAT. The maximum removal for each of the raw materials was identified based on the dosage effect.

Table 1: List of Chemical and Reagents

No.	Name of chemicals	Assay	Supplier	Purpose
1.	Sodium alginate ($C_6H_7O_6Na$)	91-106 %	R & M Chemicals, UK	Used as aqueous binder
2.	Calcium chloride ($CaCl_2.H_2O$)	≤ 99.99 %	R & M Chemicals, UK	Crosslink solution in aqueous
3.	COD reagent (Range: 500-1500 mg/L	-	Hach, USA	COD test
4.	ICP multi element standard	-	Merck, Germany	Heavy metals measurement

3. Results and discussions

Cotton dyeing wastewater sampling and characterization were carried out for a period of 12 months whereby 24 numbers of samples were collected from non-colour pit. In situ analysis including pH and temperature was measured by using Multiparameter Probe (YSI, USA). Meanwhile, COD, and colour were analyzed by using DR 6000 (Hach, USA) in the laboratory. Cu (II) was analyzed by using Ion Conductive Plasma-OES (Varian, Australia). Table 2 shows the cotton dyeing wastewater characteristics with respect to Standard B, Environmental Quality (Industrial Effluent) Regulations 2013. From the table, it can be observed that high pH values (8.06-12.78) were associated to the alkalinity of textile wastewater components. In general, textile manufacturing processes utilize

sodium salts such as hydroxide, carbonate, chloride, hypochlorite in different wet processes (Rathore, 2012). Therefore, the end product contributes high pH condition as was expected judging from the results obtained.

The concentration of COD of the cotton dyeing wastewater (1473 mg/L) was considered high and exceeded the Standard B limit of 250 mg/L. Generally, COD measures the oxygen equivalent of the organic matter content that is susceptible to oxidation by a strong chemical oxidant (Bisschops and Spanjers, 2003). High concentration of COD was attributed to the use of scouring agents that could have originated from detergents, soaps, wetting agents, defoamers and lubricants. The organic matter in the cotton dyeing wastewater was referred to the unoxidized colloidal matter from processed

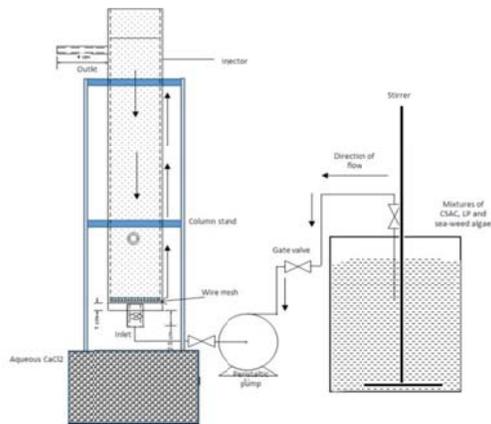pulp, cotton gum, cellulose, hemicellulose and alkali (Wang et al., 2012).

Fig. 1: Schematic illustration of experimental set-up

The presence of high COD was usually found after the fabrics have been thoroughly rinsed for the removal of surplus agents. In this condition, the wastewater might be chemically aggressive and toxic to the environment (Bisschops and Spanjers, 2003). In addition, it has been found that over 70% of the organic materials present in the textile wastewater could be determined by COD measurement that reflects the influence of bio-solid assays (Singh and Arora, 2011). The concentration of COD in this work was considered moderate compared to the result observed by Sridewi et al. (2011) who found that the COD concentrations could reach to the extent of 3190 to 21,000 mg/L. High concentrations of COD were due to wastewater generated from dyeing and printing processes.

In another report, high concentrations of COD were associated to the destruction of hydroxyl functional groups and aldehydes that originated from azo dyes (Ghaly et al., 2014). Also, COD concentrations were found to increase when dye molecules were oxidized, resulting in small organic molecular fragments such as acetic acid, aldehydes and ketones, (de Souza et al., 2010).

In measuring wastewater quality, colour is the most studied parameter because the presence of small amounts of dyes (below 1ppm) is clearly visible and influences the water environment considerably. In this work, the colour was observed having dark purple appearance with concentrations from 421 to 970 ADMI. However, it is difficult to identify the source of dyes in the wastewater component because dye solutions have a very high variability in imparting characteristics when mixed together in waste streams (Bisschops and Spanjers, 2003). Most often, major contributors of coloured wastewater usually originate from dyeing and printing processes.

Improper dye uptake as well as the degree of fixation has been considered as the major factors responsible for release of insoluble dyes in the wastewater (Singh and Arora, 2011). In terms of chemical components, almost 50% dyes used nowadays belong to azo which is the most common chromosphere of reactive textile dyes. Furthermore, the colour of direct dyes is duller than those provided by fibre-reactive dyes and the wash-fastness is poor and as much as 5 to 10% of the dyes are lost in the effluent during dyeing process (Rai et al., 2005).

Heavy metals from textile processing may enter wastewater streams in many ways such as incoming water supply, metal parts (pumps, pipes and valves), oxidizing and reducing agents, electrolytes, dyes, finishing agents as well as chemical agents (Bisschops and Spanjers, 2003). Therefore, it is difficult to determine the types of metals present in wastewater streams unless each of the textile stages is subjected to individual treatment schemes which are very costly to the operator. The average values for Cu (II) observed was in the ranges of 0.45-6.19 which exceeded the permissible limit regulated by DOE (i.e. 1 mg/L).

Smith (1986) reported that primary source of copper was found in wet processing, which indicated that about 95% of the effluent originated from dyestuff carried high copper contents. Besides, stripping agents that were mostly used in fabric repair have been found to contribute to the zinc content in wastewater streams. Despite many of the newly developed dyes are metal-free (Bisschops and Spanjers, 2003), the release of toxic metals are a result from the mixture of various textile manufacturing steps that are very difficult to deal with (Ahmaruzzaman, 2011).

3.2. One factor at a time treatment (OFAT)

The effects of individual adsorbent namely CSAC and LP were tested based on one factor at a time in order to obtain initial removal patterns from cotton dyeing wastewater pollutants. The main reason for selecting dosage effect was to determine the ability of a water sample to be adsorbed with the smallest amount of adsorbent (Yagub et al., 2014). Further, this procedure provides the most economical amount of adsorbent prior to mixing together. In addition, the range of study for the adsorbent could be determined based on this step. In this case, the shaking speed (150 rpm) and contact time (15 mins) were kept constant throughout the experimental study which followed previous works (Foul et al., 2009).

3.3. Effect of CSAC dosage

Adsorbent dosage is an important process parameter to determine the capacity of an adsorbent for a given amount of adsorbent at operating conditions. The effect of CSAC dosage towards cotton dyeing wastewater parameters is shown in Fig. 2. In addition, the wastewater volume was fixed at 150 mL throughout the study.

Table 2: Cotton dyeing wastewater characteristics

Parameters	Units	June 2012-June 2013		Standard B*
		Values	Average	
pH	-	8.06-12.78	10.7	5.5-9.0
COD	mg/L	964-2057	1473	250
Color	ADMI	421-970	572	200
Copper(II)	mg/L	0.45-6.19	1.59	1.0
Temperature	°C	31.4-45.5	36.05	40.0

From the figure, the pollutant removal increased with increasing dosage of CSAC in the ranges of 2 to 8 g/L. The best result was observed for a dosage of 8 g/L. At this dosage, about 49%, 45% and 31% of COD, colour and Cu (II) were removed, respectively. It can be inferred that CSAC displayed good COD and colour removal but low on Cu (II). This is because CSAC contained well-arranged pore structures that allowed entrapment of dye molecules as well as organic compounds from cotton dyeing wastewater sample.

This finding also conformed to a previous study, which found that effective adsorption of dye molecules formed a void-free film; masking the reliefs of particles and porosity of the aggregates (Aljeboree et al., 2014). In contrary, weak van der Waals forces exerted in the structure of CSAC have led to low intermolecular changes of metal ions, particularly for the case of Cu (II). In other words, the attractions between carbon molecule and Cu^{2+} ion were weak that restricted for the molecules to stick together. In addition, little presence of functional groups for metal ions including hydroxyl and lactone were responsible for the low affinity of CSAC towards Cu (II) adsorption (Amuda et al., 2007).

Although further increased in CSAC dosage would improve the metal ions removal (Babel and Kurniawan, 2004), the phenomenon was not observed due to the low availability of exchangeable sites on the CSAC surface. Another important finding was the high removal of colour from the wastewater sample was due to the surface charge of the carbon of CSAC. According to Demirbas (2009), depending on the nature of the dyes, chemical reaction that formed a covalent bond between the dyes atoms and that of carbon atoms which exhibits high degree of removal for coloured wastewater. In fact the shared pairs initiated stable attractive and repulsive forces between these atoms that led to higher colour removal. From the figure, it also can be seen that increasing dosage of CSAC gradually increases the removal percentage of COD, colour and Cu (II).

3.4. Effect of LP Dosage

The effect of LP dosage towards pollutants removal is illustrated in Fig. 3. The wastewater sample used was fixed at 150 mL throughout the study. Briefly, it can be observed that the removal pattern for COD, colour and Cu (II) were in the ranges of 1 to 52%. The removal trend was slightly different to that of CSAC. It can also be inferred that

higher removal for Cu by LP was dominant as the dosage increased from 2 to 8 g/L.
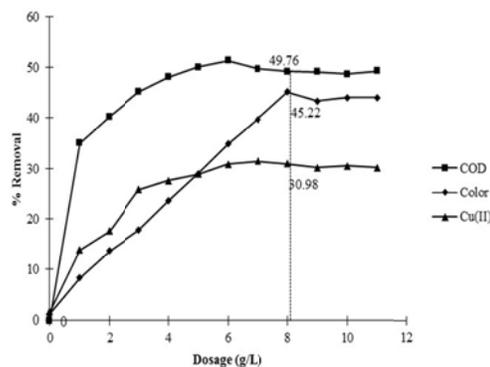

Fig. 2: Effect of CSAC dosage towards COD, colour and Cu (II) removals

High removal of Cu by LP was expected because the rough surface of LP provides solid contact with water molecules that result in chemisorptions of Cu ions (Aziz et al., 2008). Apart from that, lower initial concentration of Cu (II) (1.59 mg/L) allowed the chemisorption to occur instantly during the adsorption course (Cheng et al., 1998).

According to Shaheen et al. (2013), the sorption mechanism was responsible for the ion exchange between metal ions in the aqueous solutions and Cu^{2+} on the surfaces of $CaCO_3$ on the LP's surfaces. Therefore, the precipitation mechanism is important for the removal of Cu, which held strong affinity with increasing surface loading, accordingly. Meanwhile, gradual increase was observed for the case of COD when the LP dosage was increased from 2 to 6 g/L. Beyond 6 g/L, the removal percentage started to become uniform with small margin of additional percentage recorded. Nevertheless, it was further observed that colour removal was least influenced by LP, where the removal percentage recorded was in the range of 1 to 7% only. Between these percentages, the maximum colour removal could be achieved by LP when the dosages of 6 to 8/L g were employed (34%). Generally, some of the organic fractions in wastewater sample mainly comprises of mobilized and immobilized molecules. Thus, the removal of COD and colour correlated each other, whereby organic fractions are easier to attach to the LP surfaces rather than dye molecules in the wastewater sample. Furthermore, the wastewater component also played a vital role during the adsorption course because mixture of pollutants resulted in little removal efficiency.
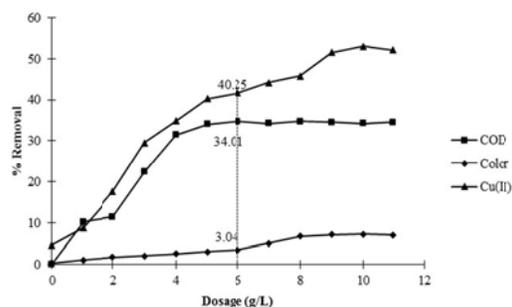
Fig. 3: Effect of LP dosage towards COD, colour and Cu (II) removals

3.5. Rheological properties of sea-weed algae

The rheological property of sea-weed algae solution such as its viscosity was carried out before the binder was mixed together with the precursors. Briefly, viscosity measurement is carried out to determine the flow behaviour where raw materials must be consistent from batch to batch (Oliveira et al., 2010). This procedure is also important in order to identify the relationship between viscosity and surface tension of a solution. For example, a high viscosity liquid requires more power to pump than a low viscosity one. In this study, sea-weed algae powder was mixed with a predetermined volume of water and the ratio was identified by the weight of sea-weed algae powder to volume of water (%w/v). Firstly, a known amount of sea-weed algae powder (g) was mixed in 25, 75, 100, 125 and 150 mL of distilled water (v). To reduce the impact of

uncontrolled factors, stirring rate and stirring period were fixed at 150 rpm for 15 minutes for every batch throughout the viscosity measurement. The density of sea-weed algae solution was obtained by using a densimeter (Blaubrand, Germany) and then compared with the density of water as the reference value. Table 3 shows the result of the viscosity measurement. Briefly, it can be observed that by increasing sea-weed algae concentration, it proportionally led to an increase in density and viscosity. When the amount of sea-weed algae was 0.5% w/v, the density was found comparable to water (1 g/cm3). In fact, uniform increments of densities were also observed when the sea-weed algae concentration was increased to 3% w/v (1.006-1.089 g/cm3). Having said that, the sea-weed algae concentration was limited to 3% w/v because the solution became very viscous; making it difficult to extrude it from the injector if the concentration studied was kept increased beyond 3% w/v. Furthermore, higher viscosity was found to reduce the mixing ability of the solution due to excess presence of alginate network chains in water molecules (Chan et al., 2010).

Meanwhile, it can be observed that by increasing sea-weed algae concentration has inversely proportional relationship to the surface tension which due to expansion of the sea-weed algae chain with water molecules (Chan et al., 2010). Fig. 4 illustrates the relationship between viscosities against shear rate.

Table 3: Rheological properties of sea-weed algae

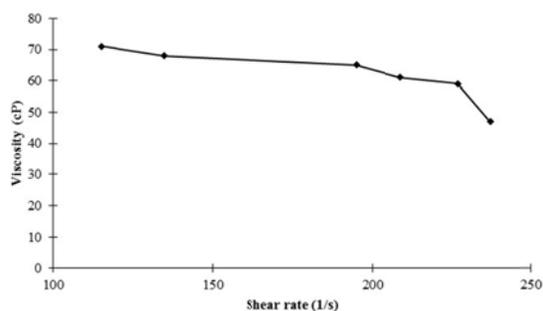| Alginate ,%w/v	Density, ρg/cm³	Viscosity, cP	Shear rate, 1/s	Surface tension, mN/m
0.5	0.999	47	237	69.10
1	1.006	59	227	59.65
1.5	1.010	61	209	53.30
2	1.024	65	195	43.44
2.5	1.067	68	135	41.02
3.0	1.089	71	115	37.14

Fig. 4: Plots of viscosity against shear rate

In general, the viscosity of sea-weed algae solution increased as the shear rate was decreased from 237 to 115/s, which confirms the pseudo plastic behavior of the suspensions (Islam et al., 2014). When the viscosity of the composite blend

was in the range of 47-68 cP, the shear rate was found to slowly decreased from 237 to 135/s. The plot also indicates that in order to maintain workable composite blend for beads injection, the viscosity must be in the range of 47 to 65 cP. This is because; higher shear rate would cause detrimental effects for the formation of spherical bead composite during injection process. Conclusively, the ideal sea-weed algae range to be used during composite adsorbent preparation is opted in the range of 1 to 3 % (w/v).

An excellent style manual for science writers is given by Young (1989).

3.6. Effect of Ca2+ concentrations

In preparing the composite adsorbent, it has been found that the concentration of calcium crosslink has important effects on the particle size and

morphology of the composite. Therefore, in order to probe the effect of calcium concentration (Ca^{2+}) towards the bead forming ability, different crosslink concentrations were tested. In this test, the same ratio for sea-weed algae from previous section was repeated to ensure minimum effect of uncontrolled factors. Besides, actual ratio for CSAC and LP were also taken into account in order to keep the consistency of the rheological test. For every batch of crosslink solution prepared, deionized water was used to dissolve the $CaCl_2$ powder. The prepared mixtures were injected from the bead injector and released into the different concentrations of crosslink solution. By visual observation, various shapes of composite adsorbent were formed under different calcium crosslink solutions.

Fig. 5 illustrates the temporal changes of bead forming ability at different crosslink molarities. Briefly, when sea-weed algae mixtures were extruded into calcium cross-linking solution, they experienced moderate swelling and subsequent shrinking and therefore they could maintain their form in a desired shape. As can be seen from Figs. 5 (a) to (f), increasing the molarity of calcium

crosslinks led to better beads formation. The spherical bead shape adsorbent was formed due to the blocks of guluronic residues that attach to Ca^{2+} cations resulting in a three dimensional network of alginate strands held together with ionic interaction (Simpson et al., 2004). In fact, a better spherical shape of composite adsorbent could be obtained by the use of higher concentration of divalent ions. As such, calcium crosslink predominantly induced the formation of a more compact composite adsorbent. This finding suggests that the diffusion of molecules through alginate based composite adsorbent depends upon the cross-linking ion concentration (Donati and Paoletti, 2009).

Fig. 6(a) shows composite adsorbent. The average bead size was 3.42 – 3.45 mm in diameter. Prior to use, the freshly composite bead had spherical shape form and rigid outer membrane (Fig. 6 (b)). Once submitted for water immersed, the composite had become bigger spherical shape which reflects water molecule water bearing ability as shown in Fig. 6.

Crosslink concentration (mM)	Physical appearance	Attribute
1.0		Elongated No consistency
1.5		Short form No consistency
2.0		Irregular bead form Short tail
3.0		Irregular bead shape Varied tail gate
4.0		Well round shape Consistent spherical bead shape and size
5.0		Oversized Inconsistent bead filling

Fig. 5: Composite adsorbent at a) 1 mM, b) 1.5 mM, c) 2.0 mM, d) 3.0 mM, e) 4.0mM and f) 5.0 mM

4. Conclusions

This study discussed the ability of individual treatment efficiency of coconut shell activated carbon and limestone powder towards COD, color and Cu(II) removals from actual cotton dyeing

wastewater. From wastewater characteristics, it has been determined that the sample analyzed exceeded the Department of Environment permissible discharge limit. Having said that, it was found that the composite adsorbent prepared was optimum prepared at dosage 8 g/L. At this dosage, about 49%, 45% and 31% of COD, colour and Cu(II) were

removed, respectively. Meanwhile, 6 g/L, of LP was found optimum to remove more than 34% of the same parameters. The results also revealed that in order to obtain spherical bead of adsorbent, 1 to 3 % (w/v) of sea-weed algae was required. Furthermore, increasing the molarity of calcium crosslinks led to better beads formation in the ranges of 3 -5 mM. The above results obtained have shown that there is possibility to produce carbon mineral composite adsorbent provided that the preparation conditions do not exceed the individual dosage threshold especially for CSAC and LP dosage. In addition, the ranges proposed in this study is proposed to be studied further towards the treatability of composite adsorbent in removing difficult parameters from cotton dyeing wastewater.
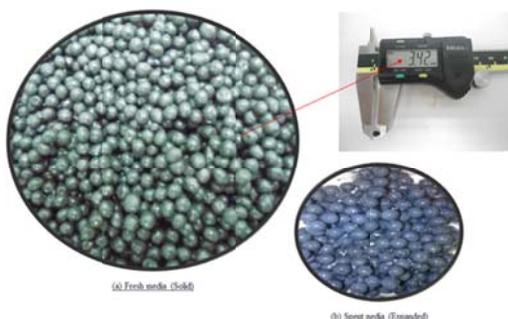

Fig. 6(a): Composite adsorbent

Fig. 6(b): Physical characteristics of fresh and spent composite adsorbent

Acknowledgment

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