

خصائص صباغة القطن بمياه الصرف وكفاءة معالجتها باستخدام قشر جوز الهند المنشط بالكربون ومسحوق الحجر الجيري

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الخلاصة

المياه العادمة الناتجة من الصناعات النسيجية غالبا ما تحتوي على مزيج من المواد الكيميائية والمذيبات والمواد المضافة التي تتطلب العديد من طرق المعالجة الفيزيائية والكيميائية والتي يمكنها التعامل مع مجموعة واسعة من الملوثات. وقد تمت دراسة تطبيق المعالجة بالامتزاز لمياه صرف النسيج لسنوات. ومع ذلك، فإن هناك بيانات محدودة للغاية متاحة بالنسبة لتطوير مركبات صديقة للبيئة مستمدة من الكربون المنشط من قشر جوز الهند ومسحوق الحجر الجيري كمواد أساسية والطحالب البحرية كمادة أساسية مساعدة على التماسك. لقد أجريت محاولة لتحديد تأثير المعالجة بالمادة المازة على وجه الخصوص لإزالة المواد العضوية الغير قابلة للتحليل البيولوجي واللون والنحاس من المياه العادمة الناتجة عن صباغة القطن. بإجراء مرحلة الامتزاز بمادة واحدة، 8 جرام / لتر من الكربون المنشط وحده كان قادرا على إزالة 49%، 45% و 31% من المواد العضوية الغير قابلة للتحليل البيولوجي واللون والنحاس من المياه العادمة الناتجة عن صباغة القطن. بإجراء مرحلة الامتزاز بمادة واحدة، 8 جرام / لتر من الكربون المنشط وحده كان قادرا على إزالة 49%، 45% و 31% من المواد العضوية الغير قابلة للتحليل البيولوجي واللون والنحاس من المياه العادمة الناتجة عن صباغة القطن. في نفس الوقت، فإن إضافة 6 جرام / لتر من مسحوق الحجر الجيري هي الأمثل لإزالة أكثر من 34% من هذه الملوثات وأظهرت النتائج أيضا أنه من أجل الحصول على حبة كروية من المادة المازة المركبة، فإن ذلك يتطلب 1-3% وزن / حجم من الطحالب البحرية. وعلاوة على ذلك، أدت زيادة المولارية من روابط الكالسيوم لأفضل تشكيل للحبيبات في نطاق 3-5 م.

Cotton Dyeing Wastewater Characteristics and its Treatment Efficiency using Coconut Shell Activated Carbon and Limestone Powder

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ABSTRACT

Textile wastewater often contains a mix of chemicals, solvents and additives which require numerous physical and chemical treatment methods that tolerate a wide range of pollutants. The 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 the 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 treatments of individual adsorbent specifically for the removal of COD, color and Cu(II) from the cotton dyeing wastewater. From the single stage adsorption procedure, CSAC dosage of 8 g/L. was able to remove 49%, 45% and 31% of the COD, color and Cu(II), respectively. Meanwhile, a 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 the 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 range of 3 - 5 mm.

INTRODUCTION

Textile industries are known as water intensive users at which the continuous increase in the demands for textile products in the domestic and export markets has been the reason for a large volume of untreated wastewater (dos Santos *et al.*, 2007). In general, every stage of textile production has its environmental impacts, from the fiber production through manufacturing until finished goods (Kamaruddin *et al.*, 2013a). The 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 the government legislation and environmental protection. The adsorption process is considered to be a superior option because of its convenience, ease of operation and simplicity of design, which makes it capable of removing heavy metals (Al-Ghouti *et al.*, 2010), color (Syafalni *et al.*, 2012), COD (Ahmad *et al.*, 2012) and organic contents from the synthetic and actual textile effluents (Ahmad *et al.*, 2013; Kamaruddin *et al.*, 2013b).

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

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

The composite adsorbent is mostly produced by mechanical mixing between the minerals and carbon compounds. This type of adsorbent is characterized by specific properties, whereby its surfaces have a mosaic characteristic that can adsorb both organic and inorganic substances simultaneously (Leboda *et al.*, 2006). Consequently, the idea of the sea-weed algae containing activated carbon and limestone particles is considered as a promising technique for dealing with the recalcitrant pollutant 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 turn from hydrophobic to hydrophilic and vice versa.

Typical Cotton Dyeing Wastewater Characteristics

Table 1 shows the cotton dyeing wastewater characteristics with respect to the Standard B, Environmental Quality (Industrial Effluent) Regulations 2013 (DOE, 2013). The standard, which has been outlined by the Department of Environment Malaysia, was gazetted under the Environmental Quality Act 1974 (amended 2009) in order to safe guard the receiving water from the industrial effluent discharge. This regulation is applicable to any premises which discharge industrial effluent or mixed effluent, onto or into any soil, or into any inland or Malaysian waters. From the table, it can be observed that the high pH values (8.0612.78-) were associated with the alkalinity of the textile wastewater components. Briefly, textile manufacturing processes utilize sodium salts such as hydroxide, carbonate, chloride, hypochlorite in the different wet processes (Rathore, 2012). 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 & Spanjers, 2003). A high concentration of COD was attributed to the use of scouring agents that could have originated from detergents, soaps, wetting agents, defoamers and lubricants. In this condition, the wastewater might be chemically aggressive and toxic to the environment (Bisschops & Spanjers, 2003). In addition, it was found that over 70% of the organic materials present in the textile wastewater could be determined by COD measurement that reflects its influence on the bio-solid assays (Singh & 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 3,190 to 21,000 mg/L. In another report, the high concentrations of COD were associated to the destruction of hydroxyl functional groups and aldehydes originated from the azo dyes (Ghaly *et al.*, 2014).

In measuring the wastewater quality, color is the most studied parameter because the presence of small amounts of dyes (below 1 mg/L) is clearly visible and influences the water environment considerably. Based on the cotton dyeing wastewater characteristics data, the color was observed having a 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 the waste streams (Bisschops & Spanjers, 2003). The improper dye uptake and degree of fixation have been considered as the major factors responsible for the release of insoluble dyes in the wastewater (Singh & Arora, 2011). Furthermore, the color of direct dyes is duller than those provided by the fiber-reactive dyes while the wash-fastness is poor and as much as 5 to 10% of the dyes are lost in the effluent during the dyeing process (Rai *et al.*, 2005).

Heavy metals from textile processing may enter wastewater streams in many ways such as through the incoming water supply, metal parts (pumps, pipes, and valves), oxidizing and reducing agents, electrolytes, dyes, finishing agents as well as chemical agents (Bisschops & Spanjers, 2003). The average values for Cu(II) observed were in the range of 0.456.19- which exceeded the permissible limit regulated by DOE (i.e. 1 mg/L). Smith (1986) reported that the primary source of copper was found in wet processing which indicates that about 95% of the effluent originated from dyestuff carried high copper contents. Despite many of the newly developed dyes are metal-free (Bisschops & Spanjers, 2003), the release of toxic metals is the result of the mixture of various textile manufacturing steps that are very difficult to deal with (Ahmaruzzaman, 2011).

Table 1. Cotton-dyeing wastewater Characteristics (Sampling location: Buffer pit)

Parameter	Unit	June 2012-June 2013		Standard B*
		Values	Average ± Standard Deviation	
pH	-	8.06-12.78	10.7 ±2.21.....	5.5-9.0
COD	mg/L	964-2057	1473 ±552.....	250
Color	ADMI	421-970	572 ±168.....	200
Copper(II)	mg/L	0.45-6.19	1.59 ±0.65.....	1.0
Temperature	°C	31.4-45.5	36.05 ±2.56.....	40.0

*Standard A is applicable to discharge into any inland within waters within catchments area, while Standard B is applicable to any other inland waters or Malaysian water (DOE, 2013)

In this first stage of work, the coconut shell activated carbon and limestone powder were tested towards pollutant removal from the cotton dyeing wastewater by batch studies which also investigated on the removal efficiency for each of the parameters. The wastewater sample was collected from the actual cotton dyeing wastewater to determine the efficiency of COD, color and Cu(II) removal in the batch studies. The rheological property of the sea-weed algae and effects of Ca^{2+} ions were studied in order to produce a spherical bead composite.

MATERIALS AND METHODS

Chemicals

All chemicals used in the study are listed in Table 2. 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 the supplier guidelines.

Table 2. List of Chemicals and Reagents

No.	Name of chemical	Assay	Supplier	Purpose
1.	Sodium alginate ($\text{C}_6\text{H}_7\text{O}_6\text{Na}$)	91-106 %	R & M Chemicals, UK	Used as aqueous binder
2.	Calcium chloride (CaCl_2)	≤ 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

Composite Mix Preparation

The composite mix preparation involved several physical and mechanical procedures which combined a known amount of CSAC and LP as suggested by Annadurai *et al.* (2002). First, the known amount of freshly CSAC and LP powder was introduced into a 500 mL beaker. A known volume of distilled water was then added and stirred with a mechanical stirrer (Ika, Germany) for 15 minutes at 50 rpm speed. Next, the beaker was heated to 80°C on a hot plate and the sea-weed algae powder was slowly added to 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 a control valve. Finally, the ejected mixtures were immersed in a CaCl_2 solution for 12 hours in order to achieve rounded and hardened beads. The schematic illustration of the experimental set-up is shown in Figure 1.

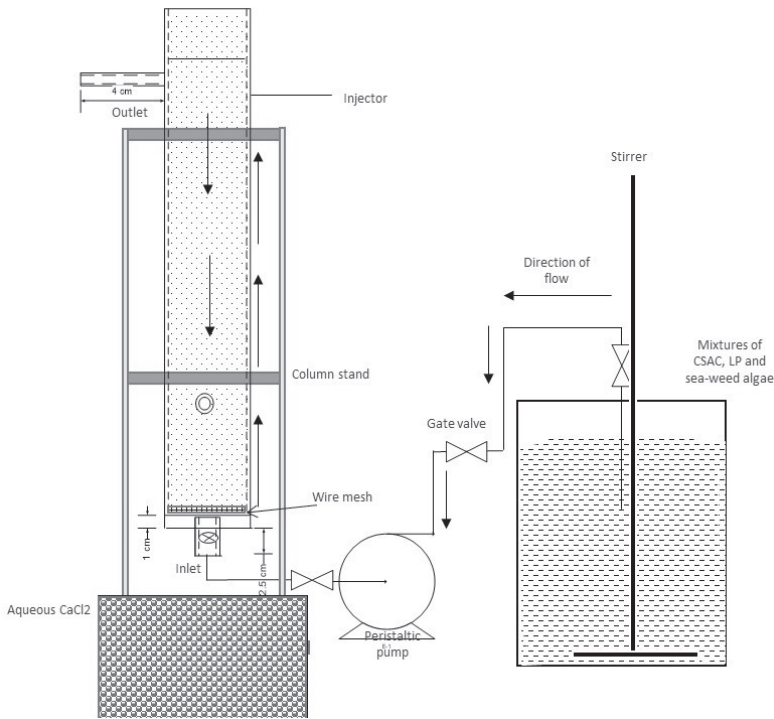


Fig. 1. Schematic illustration of experimental set-up

Batch Adsorption Studies

In this study, the treatability of CSAC and LP was individually tested via batch studies. The one factor at a time (OFAT) approach is one of the commonly used techniques 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 being investigated, which could be realized with minimum error. In this study, the performance of CSAC and LP towards the removal of COD, color and Cu(II) was tested via OFAT. The maximum removal for each of the raw materials was identified based on the dosage effect.

RESULTS AND DISCUSSIONS

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 the initial removal patterns from the cotton dyeing wastewater pollutants. The main reason for selecting the dosage effect was to determine the ability of a water sample to be adsorbed with the smallest amount of adsorbent (Yagub *et al.*, 2014). Furthermore, 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).

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 the cotton dyeing wastewater parameters is shown in Figure 2. In addition, the wastewater volume was fixed at 150 mL throughout the study. From the figure, the pollutant removal increased with the increasing dosage of CSAC in the range 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, color and Cu(II) were removed, respectively. It can be inferred that CSAC displayed good COD and color removal but low on Cu(II). This is because CSAC has been proven to contain well-arranged pore structures that allow the entrapment of dye molecules as well as organic compounds from the cotton dyeing wastewater. This finding also conformed a previous study which found that effective adsorption of dye molecules formed a void-free film masking the relief of particles and porosity of the aggregates (Aljeboree *et al.*, 2014). On the contrary, the weak van der Waals forces exerted in the structure of CSAC have led to the 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 the molecules to stick together. In addition, the little presence of the functional groups of metal ions including hydroxyl and lactone was responsible for the low affinity of CSAC towards Cu(II) adsorption (Amuda *et al.*, 2007). Although a further increase in the CSAC dosage would improve the metal ion removal (Babel & Kurniawan, 2004), the phenomenon was not observed due to the low availability of the exchangeable sites on the CSAC surface. Another important finding was the high removal of color from the wastewater sample due to the surface charge of the carbon of CSAC. According to Demirbas (2009), depending on the nature of the dyes, the chemical reaction that forms a covalent bond between the dye atoms and that of carbon atoms exhibits the high degree of removal for colored wastewater. In fact, the shared pairs initiated stable attractive and repulsive forces between these atoms that led to the higher color removal. From the figure, it can also be seen that the increasing dosage of CSAC gradually increases the removal percentage of COD, color and Cu(II).

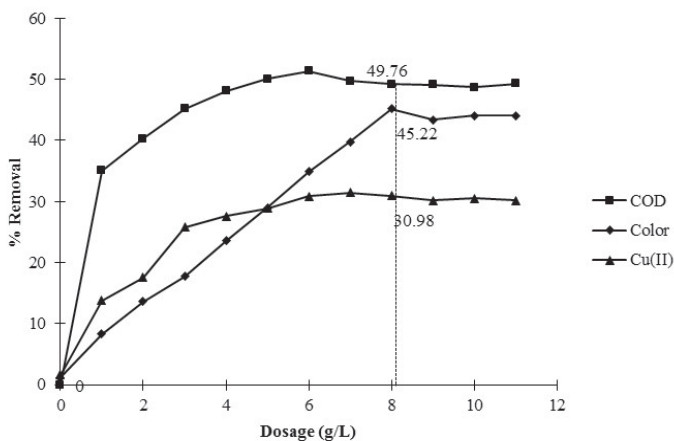


Fig. 2. Effect of CSAC dosage on COD, colour and Cu(II) removals

Effect of LP Dosage

The effect of LP dosage on pollutant removal is illustrated in Figure 3. The wastewater sample used was fixed at 150 mL throughout the study. Briefly, it can be observed that the removal pattern for COD, color, and Cu(II) was in the range of 1 to 52%. The removal trend was slightly different to that of CSAC. It can also be inferred that the higher removal for Cu by LP was dominant as the dosage increased from 2 to 8 g/L. The high removal of Cu by LP was expected because the rough surface of LP provides a solid contact with water molecules that result in the chemisorption of Cu ions (Aziz *et al.*, 2008). Apart from that, the 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 the metal ions in the aqueous solutions and Cu^{2+} on the surfaces of CaCO_3 on the LP surfaces. Therefore, the precipitation mechanism is important for the removal of Cu, which held a strong affinity with the increasing surface loading, accordingly. Meanwhile, the gradual increase was observed for the case of COD when the LP dosage 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 the color 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 color removal could be achieved by LP when the dosages of 6 to 8/L g were employed (3.04%). Generally, some of the organic fractions in the wastewater sample mainly comprise mobilized and immobilized molecules. Thus, the removal of COD and color correlated each other, whereby the 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 the mixture of pollutants resulted in little removal efficiency.

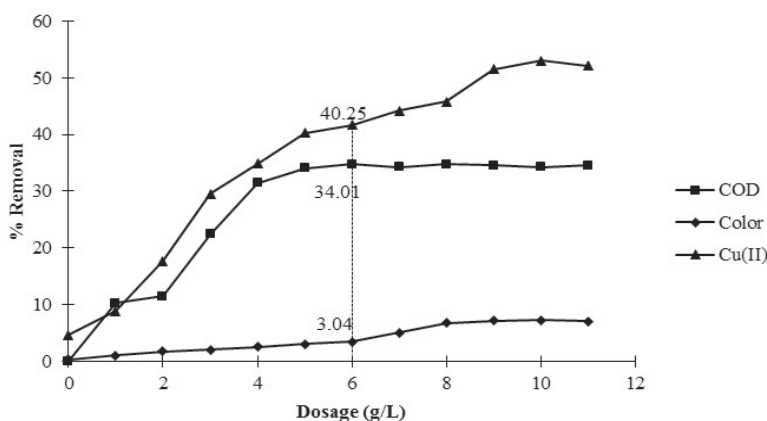


Fig. 3. Effect of LP dosage on COD, colour and Cu(II) removals

Rheological Properties of Sea Weed Algae Binder

The rheological property of algae binder such as its viscosity was carried out before the binder was mixed together with the precursors (CSAC and LP). Briefly, the viscosity measurement is carried out to determine the flow behavior where raw materials must be consistent from one

batch to another (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, the 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 the 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, the stirring rate and 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 the 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, the uniform increments of densities were also observed when the sea-weed algae concentration was increased to 3% w/v (1.0061.089- 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 be extruded from the injector if the concentration studied kept increasing beyond 3% w/v. Furthermore, the higher viscosity was found to reduce the mixing ability of the solution due to the excess presence of alginate network chains in water molecules (Chan *et al.*, 2009).

Table 3. Rheological properties of sea-weed algae

Alginate, %w/v	Density, ρ g/cm ³	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

Meanwhile, it can be observed that the increasing sea-weed algae concentration has inversely a proportional relationship to the surface tension due to the expansion of the sea-weed algae chain with water molecules (Chan *et al.*, 2009; Kamaruddin *et al.*, 2014). Figure 4 illustrates the relationship between viscosities against the shear rate. In general, the viscosity of sea-weed algae solution increased as the shear rate 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 4768- cP, the shear rate was found to slowly decrease from 237 to 135/s. The plot also indicates that in order to maintain the workable composite blend for the bead injection, the viscosity must be in the range of 47 to 65 cP. This is because a higher shear rate would cause detrimental effects on the formation of spherical bead composite during the injection process. Conclusively, the ideal sea-weed algae range to be used during the composite adsorbent preparation is opted to be 1 to 3% (w/v).

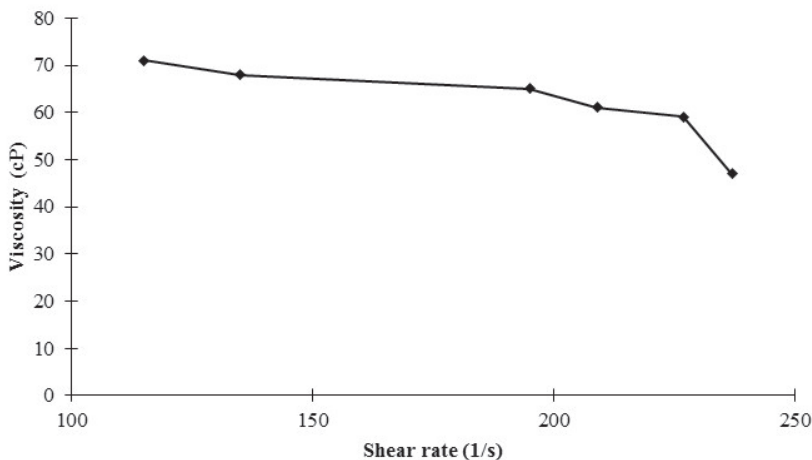


Fig. 4. Rheological properties between viscosities against shear rate

Effect of Ca^{2+} Concentrations

In preparing the composite adsorbent, it was 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 the sea-weed algae from the previous section was repeated to ensure the minimum effect of uncontrolled factors. Besides, the actual ratio for CSAC and LP was also taken into account in order to keep the consistency of the rheological test. For every batch of the 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.

Figure 5 illustrates the temporal changes of bead forming ability at different crosslink molarities. Briefly, when the sea-weed algae mixtures were released into the calcium cross-linking solution, they experienced moderate swelling and subsequent shrinking and therefore could maintain their form in the desired shape. As can be seen from Figures 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 attached to the 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, the 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 on the cross-linking ion concentration (Donati & Paoletti, 2009).




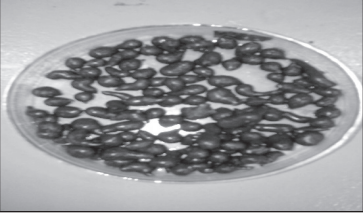
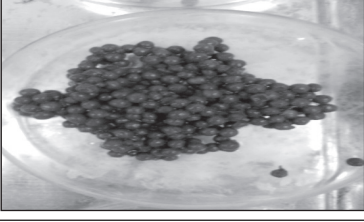
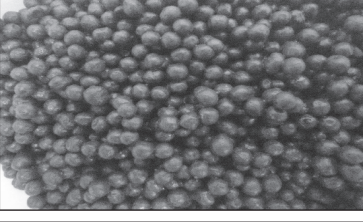
Crosslink concentration (mM)	Physical appearance	Properties
1.0		<ul style="list-style-type: none"> • Elongated • No consistency
1.5		<ul style="list-style-type: none"> • Short form • No consistency
2.0		<ul style="list-style-type: none"> • Irregular bead form • Short tail
3.0		<ul style="list-style-type: none"> • Irregular bead shape • Varied tail gate
4.0		<ul style="list-style-type: none"> • Well round shape • Consistent spherical bead shape and size
5.0		<ul style="list-style-type: none"> • 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) 4.0 mM and f) 5.0 mM

Figure 6 shows the finished composite adsorbent after repeated washing and drying prior to use. 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 (Figure 6 (a)). Meanwhile, once submitted to the batch test, the spent composite had a bigger spherical shape which reflects the water molecule bearing ability as shown in Figure 6 (b).

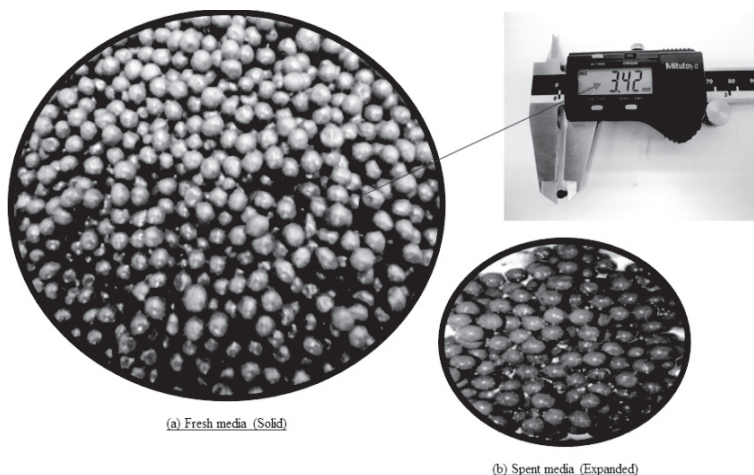


Fig. 6. Physical characteristics of fresh and spent composite adsorbent

CONCLUSIONS

This study discussed the ability of individual treatment efficiency of coconut shell activated carbon (CSAC) and limestone powder (LP) towards the COD, color and Cu(II) removals from the actual cotton dyeing wastewater. It was found that the CSAC was best prepared at a dosage of 8 g/L. At this dosage, about 49%, 45% and 31% of the COD, color 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 the spherical bead of adsorbent, 1 to 3 % (w/v) of the sea-weed algae was required. Furthermore, increasing the molarity of calcium crosslinks leads to better beads formation in the range of 3 -5 mM. The obtained results showed that there is a possibility of producing carbon mineral composite adsorbent provided that the preparation condition does not exceed the individual dosage threshold especially for the CSAC and LP dosage. In addition, the range determined in this study is to be examined further towards the capability of composite adsorbents in removing difficult parameters from the cotton dyeing wastewater.

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