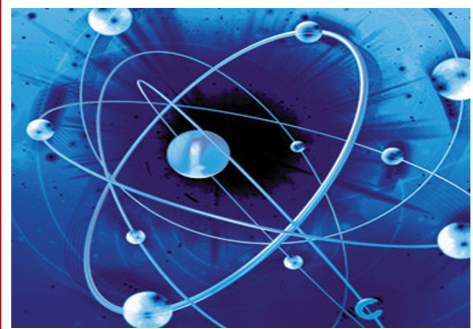
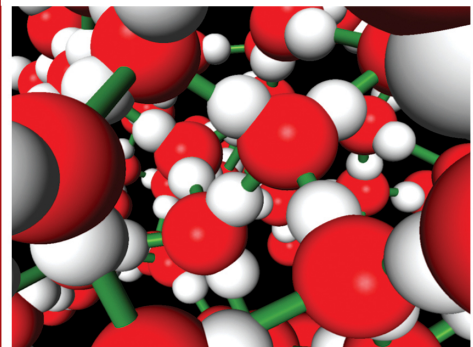
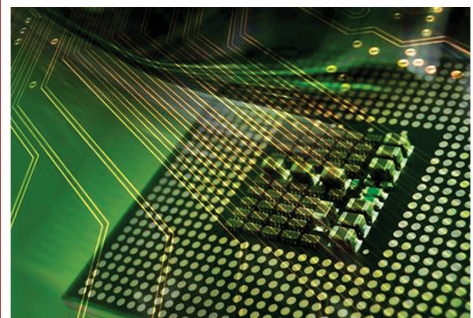
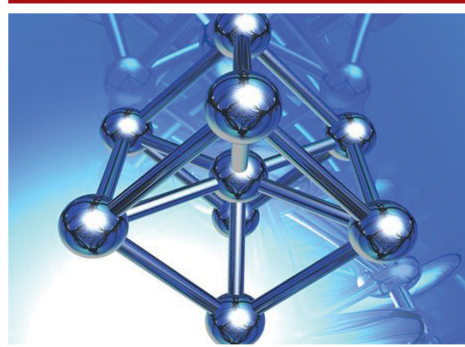


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TROPICAL SAPRIC PEAT –RUBBER AGGLOMERATES AS ADSORBENT FOR WASTEWATER TREATMENT

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ABSTRACT

Tropical sapric peat soil with severe leaching problems and poor hydraulic conductivities was converted into a functional filter media via heat treatment at 500 °C for 3 hours and agglomerated with natural rubber latex. The optimum weight ratio of peat material to rubber latex was 10:1. The peat-rubber agglomerates (PRA) had improved hydraulic conductivities, neutral pH and low organic leaching. PRA was found to be effective in the removal of chemical oxygen demand (COD) from molasses wastes and domestic wastewater. Adsorption isotherms analysis showed that the uptake of COD by PRA followed both the Langmuir and Freundlich models. Both adsorption and biological processes occurred in the removal of COD. The presence of rubber had improved the rate of bacteria growth on PRA. Sustainable removal of about 80% COD from molasses solution was achieved upon its recycled applications. This self-regenerating characteristics was proven to be due to the growth of bacteria on the surface of the adsorbent.

Keywords: Tropical peat, thermal treatment, molasses, natural rubber, peat-rubber agglomerates.

INTRODUCTION

Peat soil has been applied for the removal of various impurities from wastewaters since in the early 1980s. These impurities included oil (Mathavan and Viraraghavan, 1989; Chistova *et al.*, 1988), heavy metals (Ringqvist *et al.*, 2002), odours (Rizzuti *et al.*, 1999) and pesticides (Toller and Flaim, 1988). In addition, peat had been used for the removal of nutrients from industrial and municipal wastewaters (Dubuc *et al.*, 1986; Brooks *et al.*, 1983), from slaughterhouse wastes and from industrial and animal waste (Viraraghavan and Kikkeri, 1988). Peat had also been proven to be an efficient medium for wastewater treatment (Nichols and Higgins 2000; Arcand and Talbot, 2000). More recently, Gupta *et al.* (2008) discussed the adsorption characteristics of Irish peat moss in the adsorption of Cu and Ni. For majority of those applications, fibric peats from temperate regions were used. However, problems could arise when sapric peats are used instead due to the increased organic leaching and poor hydraulic conductivity. A highly decomposed sapric peat can have hydraulic conductivity as low as 6.9×10^{-6} cm/s (Boelter, 1969). When such peat is used as a filter media, it would give unfavourable hydraulic retention time (HRT) which can directly impacts the quality of water released to the environment (Kennedy and Van Geel, 2000). Therefore, very rare works had been done on converting sapric peat into adsorbents suitable to be used as the filter media.

Malaysian peat soil can be categorized as tropical peat soil originating mainly from plant materials. Generally, Malaysian peatlands are considered as poor agricultural lands due to their waterlogged and acidic conditions. Other uses of Malaysian peat are not well studied as compared to its temperate counterparts. One of the possibilities is its application in wastewater treatments. In contrast with the more fibrous temperate peat soil, tropical peat soil is more humified and degraded. The consistently wet and warm conditions of the environment could have accelerated the oxidative degradation of peat. These types of peat soils pose several intrinsic problems such as low chemical stability and mechanical strength, leaching of fulvic and humic acids that introduces colour into the water system, low hydraulic conductivity and difficult regeneration. Sustainable use of tropical peat soil as an organic coagulant is earlier reported by this research group (Nawi and Ibrahim, 2005; Helal Uddin *et al.*, 2008). Conversion of tropical peat soils especially the sapric types into filter media for wastewater treatments therefore needs pretreatment. Nawi *et al.* (2004) had described a thermal treatment process of some Malaysian peat soil. Thermally treated peat could solve the organic leaching and poor adsorbent properties but it is still not feasible to be used as the filter media due to its poor hydraulic conductivity.

Chan and Lin (2006) blended peat material with PVA to prevent cracking and compaction thus avoiding higher bed's head loss and uneven flow distribution. Instead of synthetic polymer, biopolymer such as natural rubber can be used for a similar purpose. Natural rubber latex was

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Table 1. Selected characteristics of Malaysian raw and thermally treated peat soils. Thermal treatment was done according to Nawi *et al.* (2004).

Parameters	Raw Peat	Thermally treated Peat (TP)	Raw BP	Thermally treated Peat (TP2)
pH	4.36 -4.50	6.50 -7.00	3.38 -3.50	6.70 -7.10
Ash, wt%	33.6 ± 0.6	65.5 ± 0.4	11.0 ± 0.4	16.5 ± 0.5
Volatile matter, wt %	66.3 ± 0.2	34.3 ± 0.2	86.7 ± 0.5	84.7 ± 0.2
Organic Carbon (%)	20.63	15.77	21.59	4.53
CEC (meq/100g)	104 ± 2	0.88 ± 0.06	143 ± 1.0	0.06 ± 0.01
Color Leaching (Hazen unit)	68 ± 3	2.5 ± 0.2	102 ± 2	2.5 ± 0.2
COD leaching,mg/L	24 ± 2	5 ± 1	69 ± 4	2 ± 1
BET Surface area, m ² /g *	4.39	19.8	0.63	2.54
Average Pore Diameter, Å *	193.48	51.1	214.34	92.12
Hydraulic conductivity, cm/sec	1.30 x 10 ⁻³ ± 1.0 x 10 ⁻⁴	1.65 x 10 ⁻³ ± 1.0 x 10 ⁻⁴	3.8 x 10 ⁻⁴ ± 3.0 x 10 ⁻⁵	4.5 x 10 ⁻⁴ ± 5.0 x 10 ⁻⁵
Langmuir monolayer capacity, Q _o , (for RR12), mg/g *	4.45	8.00	0.45	1.62

*Analysis was done without replicates.

Table 2. Langmuir and Freundlich parameters of adsorption by rubber-latex peat pellets prepared from thermally treated Gunung Jerai peat.

a	Types of samples	Constant, 1/n	Constant, K (L/g)	Correlation coefficient
	Domestic wastewater	0.025	1.34	0.99
	Molasses	0.031	0.16	0.99
	Textile dyes (RR12)	0.007	2.89	0.97

Langmuir isotherms

b	Types of samples	Monolayer capacity, Q _o (mg/g)	Langmuir constant, b (L/g)	Correlation factor
	Domestic wastewater	3.43	0.015	0.98
	Molasses	14.99	0.002	0.99
	Textile dyes(RR12)	10.47	0.385	0.99

Freundlich isotherms

selected as the binder due to its good compatibility with peat soil and excellent adhesiveness. It is also non toxic and suitable for bacteria colonization (Atagana *et al.* 1999). It has a high resistance against tear and abrasion and also quite resistant to microbial degradation (Roya *et al.*, 2006). In another study our research group has successfully demonstrated the technique of using rubber latex to prepare powder activated carbon pellet as a filter medium. It was reported that the filter could effectively remove COD and ammonia nitrogen from the fish wastewater (Helal Uddin *et al.*, 2007).

This work describes the conversion of tropical sapric peat soil into adsorbents with highly improved hydraulic conductivity and very minimal leaching problems for the removal of dissolved organics. This is realized by the agglomeration of the thermally treated peat powders with natural rubber latex. Biodegradable molasses wastewater,

domestic wastewater and solutions of non-biodegradable anionic dye, Reactive Red 12 (RR12) were used as model polluted water containing dissolved organic matter.

MATERIALS AND METHODS

Peat samples and reagents

Peat samples were obtained from Gunung Jerai (GJ) in the northern region and Batu Pahat (BP) in the southern region of West Malaysia at a depth of 0.5 m. The samples were air dried and ground into powder using a mechanical grinder. No attempt was made to separate peat particles into different sizes. High ammonia grade latex (Centrifuge Latex 60 % DRC) was purchased from *Kedahtex, Malaysia*. Molasses waste was obtained from Malayan Sugar, a sugar processing factory located in Seberang Prai, Malaysia. Reactive red 12 (RR12), C.I. 18156 was obtained from *Ciba-Geigy*. Domestic

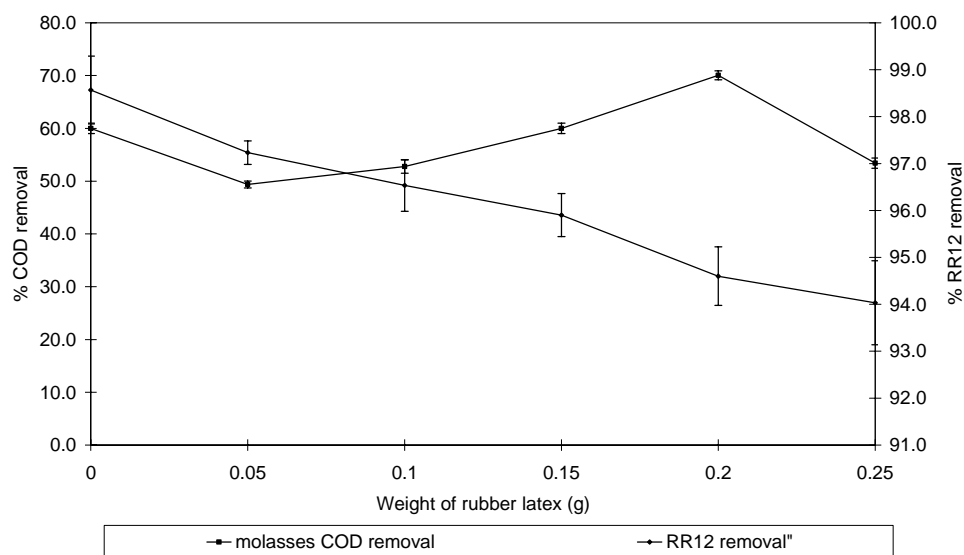


Fig. 1. The effect of the amount of natural rubber latex in the peat rubber agglomerates (PRA) and their respective application in the removal of COD from molasses solution (initial COD 265 mg/L) and RR12 (initial concentration of 200 ppm). The weight of thermally treated peat used was kept constant at 2 grams. (Mean \pm S.D, n = 3)

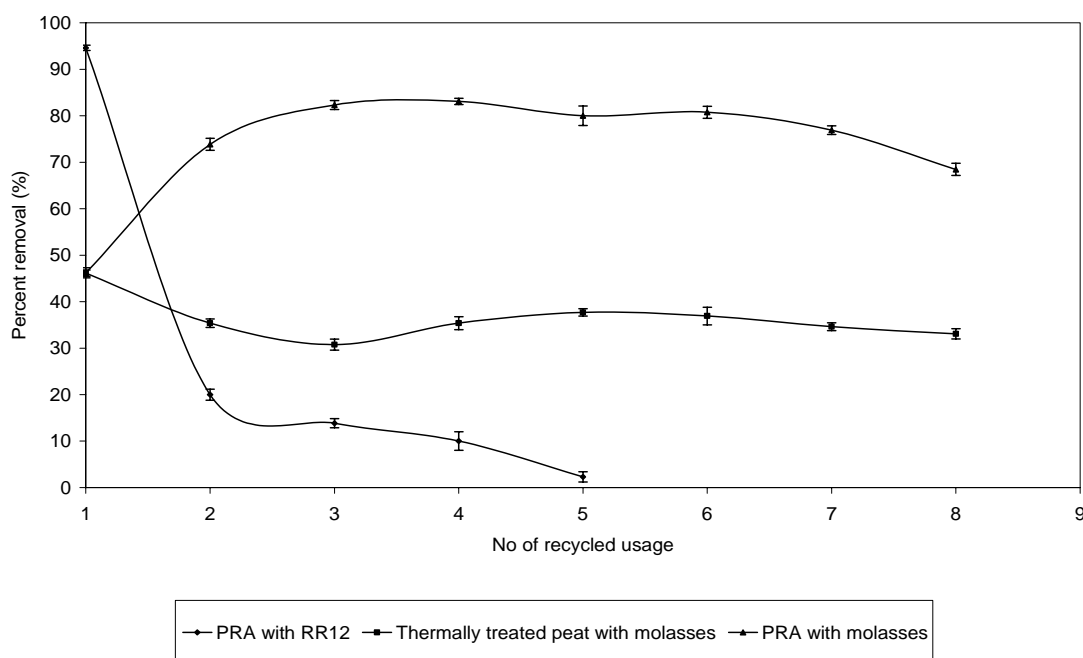


Fig. 2. Plots of percent removal uptake of COD upon recycled usage of peat-rubber agglomerates (PRA) on molasses solution, thermally treated peat without rubber on molasses solution and PRA on non-biodegradable textile dye reactive red 12 (RR12). (Mean \pm S.D, n = 3)

wastewater was collected from a sum within an activated sludge treatment facility of Universiti Sains Malaysia. Other chemicals used were of analytical grades.

Physical and chemical characterization of peat samples

Percentage of total organic and ash content were carried out by using the dry ashing methods at 600°C in a carbolite muffle furnace (Papp and Harms, 1985). The

percentage of ash and organic content were calculated from the weight of residue and the weight lost, respectively. The measurement of pH for peat samples was done by shaking 3 gm ground, air-dried peat in 50 ml distilled water according to ASTM method (ASTM, 1971). The surface area of peat samples were analysed based on the adsorption and desorption of nitrogen on peat by using ASAP 2000 porosimeter.

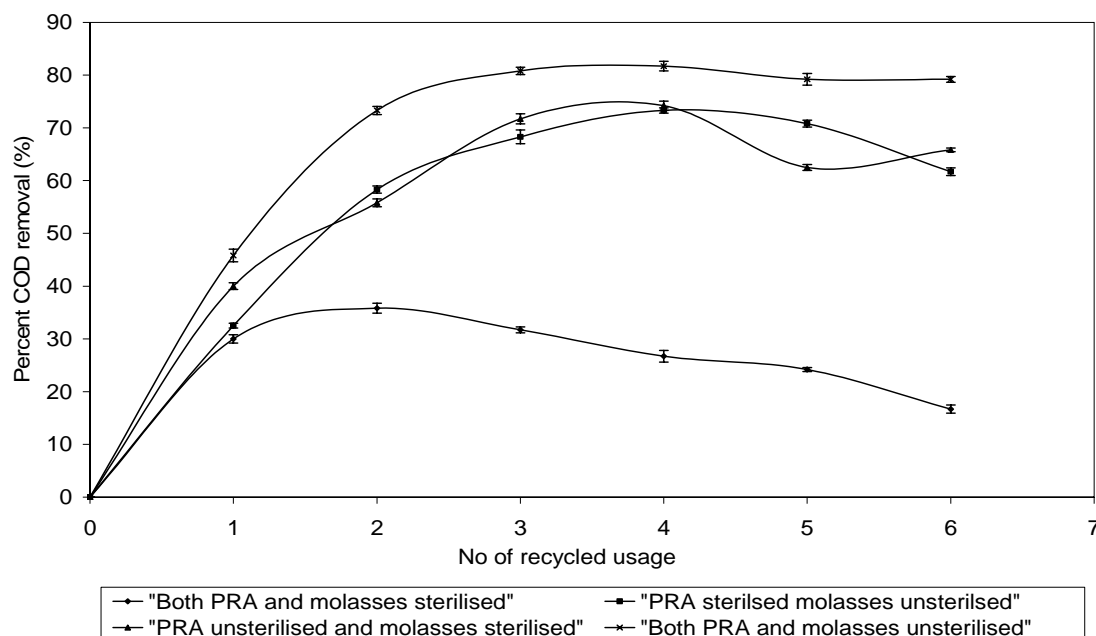


Fig. 3. The effect of sterilization on either peat-rubber agglomerates (PRA) or molasses solution or both on the efficiency of COD removal upon recycled usage of PRA. (Mean \pm S.D, n = 3)

The leaching of peat samples was conducted by shaking 2 gm each of raw air dried peat or thermally treated peat samples in 25 ml distilled water in a 150 ml conical flask for 30 min at 350 osc min^{-1} . The water from each sample was then filtered using the fritted glass filter funnel and its COD value measured using spectrophotometry method according to the HACH procedures (HACH, 1992). The sample was also used to measure color (Lovibond with filter disc CAA and CAB). Cation exchange capacity (CEC) was analyzed via the method given by Heikkinen *et al.* (1995). Hydraulic conductivity values were obtained using the method outlined by Walmsley (1977).

Preparation of peat-rubber agglomerates (PRA)

Thermal treatment was done according to the method of Nawi *et al.* (2004). Natural rubber latex ranging from 0.05 – 0.30 gm were each placed in their respective 100 mL beakers. To each beaker was added 4 mL of distilled water and the mixture was thoroughly mixed until each becomes a homogeneous emulsion. To each of these emulsions was added 2.0 gm thermally treated peat sample. Mixing of rubber latex and treated peat samples were done manually with spatula until small agglomerates of about uniform size was obtained. The peat-rubber agglomerates (PRA) were then soaked in 10% $\text{Ca}(\text{NO}_3)_2$ solution for about 30 minutes. Finally, the agglomerates were cleaned by washing generously with tap (can we put distilled water or plain water) water and stored without drying in a closed container prior to use.

Molasses solution and domestic wastewater samples

Molasses stock solution was prepared by dissolving about 1 gram molasses waste in 400 mL distilled water in 1L volumetric flask and was finally filled up to the mark with distilled water. The solution was then filtered with Whatman no. 42 filter paper and analyzed for its chemical oxygen demand (COD) (HACH, 1992). The 1000 mg/L COD solution was achieved by either diluting the prepared solution with distilled water or adding more molasses waste. Once achieved, this stock solution was stored in refrigerator below 4°C. Solutions of molasses waste with various initial COD values were prepared by diluting this stock solution as required. The expected value was later confirmed by determining the COD of the diluted sample prior to the study and determined value was used as initial COD value of the molasses waste. Domestic wastewater samples were obtained from the sewage collection sump of an activated sludge treatment facilities within Universiti Sains Malaysia.

Adsorption studies

Adsorption studies were conducted by shaking the peat molasses by using a wrist action shaker SF1 (Stuart Scientific). For the determination of equilibrium times for the adsorption of COD on peat samples, a series of 2.0 gm peat each with 25 mL of molasses solutions (initial COD value of 250 mg/L) or domestic wastewater was shaken in 125 mL conical flasks at 300 osc min^{-1} at different contact times. For adsorption isotherms, 2.0 gm peat soil samples

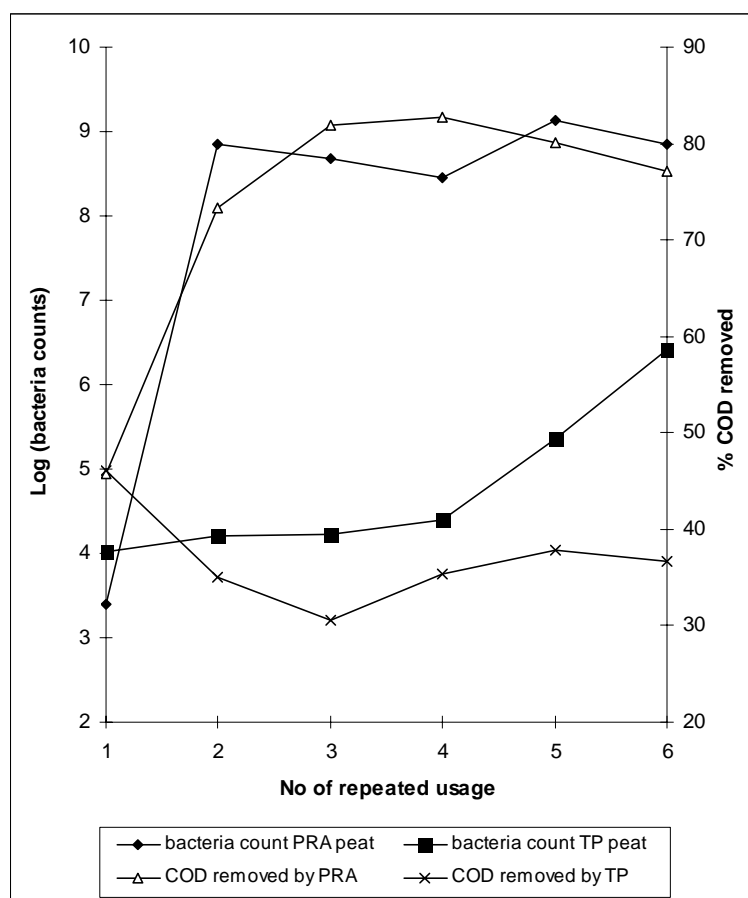


Fig. 4. The effect of bacteria counts on the reduction of COD by PRA and TP peat samples. There is an apparent correlation between bacteria counts and COD removal. Since the bacteria counts of PRA was much higher than TP, the COD removal was more efficient and sustainable close to 80% after second repeat usage.

were each shaken in 25 mL molasses solution with different initial COD concentrations for one hour. The adsorption data was plotted according to the linearized Freundlich and Langmuir equations.

Determination of self-regeneration capability of peat samples

2.0 gram samples from both the thermally treated peat and PRA were each shaken with 25.0 mL of molasses solution with initial COD of 270 mg/L at 350 osc/min in 125 mL conical flasks that are covered with parafilm for 8 hours. A blank sample containing only 25.0 mL molasses solution with similar concentration was also prepared and shaken in the same manner. Each solution was then filtered using Whatman no. 42 filter paper and their respective COD were determined. The filtered soil was kept moist and used for the second time using similar conditions. This process was repeated using the same peat samples but with new batches of molasses solution up to 8 times. Experiments with sterilized samples were done in similar manner as described in the above section. Sterilization process was done by placing samples in an autoclave (Hariyama, Japan) at 121°C, 15 psi for 15 minutes (APHA, 1995). Four sample combinations were

used namely: (i) Both PRA and molasses solution that were sterilized. (ii) PRA with only molasses solution sterilized, (iii) Sterilized PRA with non-sterilized molasses solution and (iv) Both PRA and molasses solution were not sterilized.

Bacteria counting

Bacteria counting was done for the molasses solution and on both heat treated peat samples and PRA after each successive recycled usage for the removal of COD from molasses solution as described in the above section. Each isolated peat samples was stored in a 500 mL screw-cap bottle containing 200 mL sterilized water. This gave a dilution factor of 1:100. Bacteria counting was then done using the pour plate method (APHA, 1995).

RESULTS AND DISCUSSION

As indicated by Table 1, there were four basic problems associated with Malaysian raw peat soils namely severe leaching of dissolved organic matter (based on COD and color leaching), extremely low hydraulic conductivity, low surface areas and low pH. It was also observed that, the higher the organic content of peat sample, the greater

was the color and organic leaching (BP sample). The effect of thermal treatment under closed but not air tight container produced peat samples with higher ash content and lower combustible matter. The majority of the combustible matter of the thermally treated GJ peat (GJT) is made up of organic carbon. Thermally treated BP sample (BPT) was more carbonized than GJT sample since its combustible matter contained very low percentage of organic carbon. A significant drop in cationic exchange capacity (CEC) was observed for both cases indicating that majority of their humic acid components had been destroyed or transformed to other forms. The BET (Brunauer, Emmett, and Teller) surface area for both peat samples improved with the thermal treatment. Since Langmuir monolayer capacity, Q_0 , for anionic dye RR12 of GJ sample was more than 15 times better than BP sample, this study was focused on GJ peat sample. However, as shown by Table 1, thermal treatment did not improve the hydraulic conductivities of the peat samples even though there was a significant drop in COD and color leaching. In order to solve this problem, the thermally treated peat powder was agglomerated with natural rubber latex.

The generated peat rubber agglomerates (PRA) had sizes ranging from 0.5 -1.0 cm. Optimization study of the ratio of latex to thermally treated GJ peat was done by monitoring the removal of COD from a diluted molasses wastewater sample by the prepared PRA using contact time of 8 hours (selected based on time-equilibrium study of a preliminary sample or optimized in a preliminary study). Addition of rubber to thermally treated peat powder to form PRA initially reduced the COD uptake. Increasing the rubber content however resulted in a steady increase of COD removal until an optimum ratio of 0.20 gm latex per 2.0 gm of thermally treated peat was reached as shown in figure 1. The initial drop in COD uptake was due to the increased in particle size of peat from the effect of agglomeration and also the coating of rubber on its surface. The steady increase of COD removal between 0.05 -0.2 g of added rubber was due to the removal of dissolved organic matter by additional mechanisms other than surface adsorption such as biological activities.

Beyond the optimum weight of 0.20 gm of rubber additive, a sudden decrease in COD removal was noted. This observation was due to the excess rubber that caused reduction of the adsorption process because of the shielding effect of the peat surfaces. This trend was not observed with non-biodegradable impurities such as textile dye. When a textile dye such as reactive red 12 (RR12) was used instead of molasses, a steady decrease in the uptake of the dye with increasing weight of added rubber was observed. Each additional rubber additive would increase the shielding effect of the peat surface thus reduced the effectiveness of the surface adsorption of the dye molecules. However, in all cases, the PRA

samples were still effective in removing the anionic dyes with the lowest value of uptake (at 0.25 g rubber latex) at 94.0 %. The optimum ratio of peat material to rubber latex was therefore selected at 10:1.

Adsorption isotherm studies were done using optimized PRA to determine their adsorption characteristics. The data were then fitted into linearized equations of both the Langmuir (equation 1) and Freundlich models (equation 2) where C_e is the concentration at equilibrium condition, q_e is the mass of molecules adsorbed per unit mass of adsorbent (mg/g), Q_0 the maximum amount of the adsorbate per unit mass of adsorbent to produce a monolayer coverage (mg/g), b is the langmuir constant (L/g), K is the Freundlich constant and $1/n$ is the heterogeneity factor.

$$C_e/q_e = C_e/Q_0 + 1/Q_0b \quad (1)$$

$$\text{Log } q_e = 1/n \text{ log } C_e + \text{log } K \quad (2)$$

Modes of adsorption fit both Langmuir and Freundlich as shown by the respective correlations values as given in Table 2. PRA had a Langmuir monolayer capacity (Q_0) of 14.99 mg/g for molasses, 3.43 mg/g for domestic wastewater and 10.47 mg/g for RR12 dye. This value was not significantly different from Q_0 of 15.20 mg/g molasses adsorption for the non agglomerated thermally treated peat. The Q_0 value for RR12 was even bigger than Q_0 value of GJT. Therefore, agglomerizing peat with natural rubber did not give the undesirable effect of reduced efficiency in adsorption capacities. A low $1/n$ value obtained for each case would mean that it is more suitable as a filter medium rather than as a batch-mode medium.

As stated earlier, the improved removal of COD from molasses or domestic wastewater solutions occurred via both adsorption and biological activities. In order to verify the presence of these biological activities, the same batch of PRA sample was recycled for use with several different fresh batches of molasses and domestic wastewater solutions. In this study, each solution was shaken with the respective peat samples for up to 8 hours. As shown in figure 2, the efficiency of COD removal (or dissolved organic matter) by PRA was not reduced upon its repeated usage with fresh new batches of molasses solutions. Instead, the COD removal increased after the first application and was more or less maintained for the entire duration of repeated applications. Thermally treated peat without rubber (GJT) showed a decrease in the uptake on the second usage and was maintained throughout at a lower percent removal. When a non-biodegradable anionic RR12 dye was used as pollutant sample, pollutant removal decreased with each repeated usage and eventually reached a value close to zero after the fifth reuse. Since no biodegradation occurred for such pollutant, each recycled usage would continuously reduce

the adsorption capacity of PRA so that after the fifth cycle it became completely exhausted. However molasses were biodegradable in nature. The maintenance of COD uptake with no apparent saturation point suggests the existence of bioactivity besides the adsorption process. These biological activities helped to clean-up the adsorption sites for incoming new pollutants to enable the peat-rubber agglomerates to sustain the COD removal efficiency. Comparison between PRA and GJT indicates that the added rubber significantly improved the efficiency of COD removal.

In order to verify further the effect of biodegradation occurring on the surface of PRA, experiments involving sterilization of both molasses waste and adsorbent material was done. When both molasses solution and PRA were sterilized, very poor removal of COD occurred upon recycled usages (Fig. 3). The efficiency of COD removal was reduced after each cycle of application, indicating that adsorption was the dominant process and bioactivity was very low. Regeneration of the adsorption sites therefore did not occur as fast as was expected. Better results were obtained when either one of them was not sterilized. The best result was obtained when both molasses solution and PRA were not sterilized. This observation supports the earlier conclusion that sustainable COD removal efficiency of PRA was due to the combination of adsorption and biological degradation processes.

Atagana *et al.* (1999) had noted that rubber and rubber wastes have been known to support microbial growth whereby *Pseudomonas*, *Bacillus sp.* and *Arthrobacter sp.* were proven to exist within the wastes of the rubber processing industries. Oiki *et al.* (1996) also reported that natural rubber serum powder had a marked growth stimulating effects on bifidobacterium bifidum even when a rich medium was used. Natural rubber waste serum from coagulated skim latex is known to be nutritionally rich in proteins, sugars, lipids, inorganic and organic salts which support the growth of bacteria. In this work, as shown in figure 4, the presence of rubber improved the bacteria growth rate within the PRA materials whereby a marked increase in the bacteria counts was observed. The bacteria counts increased to a steady state level after the first recycled usage. The bacteria counts for the GJT sample on the other hand had a significant increase in values after only the fourth recycled usage with its largest value of 1.70×10^8 counts lying much lower than that of PRA. Therefore it can generally be concluded that the bacteria growth increased with repeated application of the PRA samples and the growth rate was better than the GJT samples. As shown in figure 4, the growing numbers of bacteria counts on the adsorbent surface was responsible for the improved uptake of COD by PRA over its repeated applications since the curve for bacteria counts and COD removal follow a similar trend. The poor COD removal

by GJT samples was due to the longer lag period that occurred up to the fourth recycled usage. The results of the above experiments provide a clear explanation for the sustainable uptake of COD from molasses upon repeated applications of the PRA adsorbents.

Evaluation of hydraulic conductivities of PRA adsorbent gave a value of 0.227 cm/sec. This is about 174 times better than the raw peat soil. Besides low leaching and improved hydraulic conductivities, the presence of rubber had induced higher bacteria activities that helped the adsorbent to be self-regenerative. The possible role of rubber here could be to provide attachment sites for bacteria growth. Raw natural rubber is a macromolecular isoprenoid. Non rubber constituents may include proteins, lipids, carbohydrates, resins and inorganic salts. The presence of these constituents may help in the promotion of rapid bacteria growth on the surface of the PRA adsorbent. As seen from Fig. 4, introduction of rubber into the peat system has increased bacteria growth by 2- 4 folds. This phenomenon apparently enabled PRA adsorbents to be self regenerative for sustainable usage in the removal of biodegradable impurities. With good hydraulic conductivity, effective COD removal and no color leaching, PRA has a very good potential to be used as a filter media for wastewater treatment.

CONCLUSIONS

Sapric tropical peat soils with severe leaching problems and poor hydraulic conductivities was converted into an effective adsorbent via simple thermal treatment and agglomeration with natural rubber latex.. This thermally treated peat has been shown to have minimal leaching problems and improved adsorption capacity (Nawi *et al.*, 2004). Agglomeration of this thermally treated peat with natural rubber latex had significantly increased its hydraulic conductivities by at least 174 times. The optimum ratio of peat material to rubber latex was 10:1. Addition of rubber did not significantly drop the adsorption capacity of the thermally treated peat. Adsorption isotherms analysis proved that the uptake of COD and anionic dyes followed both the Langmuir and Freundlich models. The low $1/n$ value indicates that the adsorbent is more suitable for use as a filter medium rather than the batch mode medium. The removal of biodegradable pollutants occurred via both adsorption and biological activities. Since the presence of rubber improves the bacteria counts of the adsorbent by 2-4 folds, the uptake of COD by PRA was much better than GJT. Furthermore, PRA exhibited self-regeneration behaviour due to bacteria activities that free-up the adsorption sites for further uptake of the pollutants. This self regeneration capability however did not occur with non-biodegradable pollutants. With its relatively high hydraulic conductivity, PRA has a very good potential to be used as a filter media for the filtration of wastewater.

In conclusion, sapric peat can be actually processed into a functional adsorbent suitable as filter media through thermal treatment and agglomeration with natural rubber latex. Its application as the filter media to treat domestic wastewater is currently being studied.

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