African Journal of Biotechnology Vol. 9(38), pp. 6233-6243, 20 September, 2010
Available online at http://www.academicjournals.org/AJB
ISSN 1684–5315 © 2010 Academic Journals

Review

Treatment of wastewater from rubber industry in Malaysia

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Accepted 26 March, 2010

Presently, Malaysia is the third largest rubber producer in the world, whereby the rubber industry is an economically and socially significant industry. Rubber industry consumes large volumes of water, uses chemicals and other utilities and produces enormous amounts of wastes and effluent. Discharge of untreated rubber effluent to waterways resulted in water pollution that affected the human health. With a new global trend towards a sustainable development, the industry needs to focus on cleaner production technology, waste minimization, utilization of waste, resource recovery and recycling of water. The present work aims at highlighting various technologies that currently have been used for treatment of rubber effluent in Malaysia. The work introduces the basis of these processes including their benefits and also problems. It also adheres to the future trends of rubber effluent treatment in Malaysia by reviewing various treatment technologies for natural rubber industry implemented by Thailand, the world largest rubber producer. These new and effective effluent treatment methods would minimize environmental pollution of rubber industry and bring it to become sustainable and environmental friendly.

Key words: Rubber industry, effluent, waste management, Malaysia.

INTRODUCTION

Natural rubber is an elastic hydrocarbon polymer that is originally derived from a milky colloidal suspension, or latex of *Hevea brasiliensis*. The purified form of rubber which can also be produced synthetically is chemical polyisoprene. Natural rubber is extensively used in various applications and products (Sun, 2004). Today, 70 -80% of produced raw rubber in the world supply in south-east Asia, comes mainly from Thailand, Malaysia and Indonesia (Lonholdt and Andersen, 2005; Xiaofei, 2008). Main export of Malaysian products includes electronic equipment, petroleum and petroleum products, palm oil, wood and wood products, rubber and textile (Usa, 2007). Rubber plays an important role in Malaysian's economy and about 30% of foreign exchange revenue derived from this crop (Shacklady, 1983; Hutagalung, 2003; Anitha et al., 2007). However, some changes in land use were raised in the mid-80s and large areas of rubber field were converted for industrial, commercial and residential uses (Vijayaraghavan, 2008a, b). More tendencies were also done towards the plantation of lucrative crops likes oil palm and cocoa (Choo et al., 2003). Due to this, a gradual decrease occurred in raw natural rubber production. Therefore, It caused a decline to Malaysian‘s status from first to third and ranked it after Thailand and Indonesia (Vijayaraghavan, 2008a). The natural rubber statistic (2008) for Malaysia and Thailand is shown in

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Abbreviations: EQA, Environmental quality act; **UASB,** anaerobic sludge blanket reactor; **SRR,** sulphate reduction reactor; **PNSB,** purple non sulphur photosynthetic bacteria; **CW,** constructed wetland; **VF,** vertical flow; **SSF,** subsurface flow; **ORP,** oxidation-reduction potential; **BAS,** batch activated sludge; **DOE,** Department of Environment; **RRIM,** Rubber Research Institute of Malaysia; **BOD,** biological oxygen demand; **HRT,** hydraulic retention times; **COD,** chemical oxygen demand; **TDS,** total dissolved solids.

Table 1. Rubber industry in Thailand and Malaysia (Hutagalung, 2003; Kantachote and Innuwat, 2004; Puetpaiboon et al., 2005; Chaiprapat and Sdoodee, 2007; Department of Statistics, Malaysia, 2008; Association of Natural Rubber Producing Countries, 2009).

Factor	Thailand	Malaysia
Area under rubber plantation (million hectares)	2	1.3
Natural rubber production in year (million tons)	3.09	1.072
Global supply of natural rubber (percent)	33.5	10.7
Number of rubber factories	700	357

Table 2. Characteristics of process effluents from rubber processing (Chua and Garces, 1992; Guha, 1995; Bacon, 1995; Hutagalung, 2003; Choo et al., 2003; Tekasakul and Tekasakul, 2006; Chaiprapat and Sdoodee, 2007; Rungruang and Babel, 2008; Vijayaraghavan et al., 2008a).

Parameter	Typical range
pH	3.7 - 5.5
Biological oxygen demand	1500 - 7000
Chemical oxygen demand	3500 - 14000
Suspended solids	200 - 700
Total nitrogen	200 - 1800
Sulphate	500 - 2000

All units are mg/l, except pH.

Table 1 (Hutagalung, 2003; Kantachote and Innuwat, 2004; Puetpaiboon et al., 2005; Chaiprapat and Sdoodee, 2007; Department of Statistics Malaysia, 2008; Association of Natural Rubber Producing Countries, 2009).

Since the production of rubber products from natural rubber needs large amount of water for its operation, the rapid growth has produced large quantities of effluent from this processing (Leong et al., 2003; Rungruang and Babel, 2008). This effluent includes wash water, small amounts of uncoagulated latex and serum with small quantities of protein, carbohydrates, lipids, carotenoids and salts. The characteristics of rubber wastewater are presented in Table 2 (Chua and Garces, 1992; Guha, 1995; Bacon, 1995; Hutagalung, 2003; Choo et al., 2003; Tekasakul and Tekasakul, 2006; Chaiprapat and Sdoodee, 2007; Rungruang and Babel, 2008; Vijayaraghavan et al., 2008a).

According to Department of environment (DOE, 2000), the biggest sources of industrial water pollution in Malaysia are food and beverage producers, chemical based industries, textiles, paper, palm oil and rubber processing (Shirkie and Ching, 1983; Usa, 2007; Iyagba et al., 2008). 14.1% of the 2292 industries in Malaysia which identified as major sources of water pollutants are rubber producing industries (DOE, 1991). The main sources of rubber wastewater in Malaysia are skim, latex serum, uncoagulated latex and washings from the various processing stages (Abdul Rani, 1995). In average, 20 tons of rubber and 410 thousand litres of effluent per day is produced by rubber factory. Some environmental pollution has been reported due to daily discharge of about 80 million litres of untreated rubber effluent to near streams and rivers in Malaysia (Hutagalung, 2003; Tekasakul and Tekasakul, 2006; Rungruang and Babel, 2008).

The Malaysian Government instituted a set of environmental regulations that are included in the Environmental Quality Act (EQA) of 1974, and its subsequent amendments in 1985 and 1996 (Yassin, 2008).

In Malaysia, the legislative approach in water quality management and raw natural rubber industry was established in 1977-1978 (Chua and Garces, 1992; Daud, 2005; Usa, 2007). The effluent standards set by DOE, are given in the Table 3 (Choo et al., 2003).

Without proper treatment, the discharge of wastewater from rubber processing industry to the environment may cause serious and prolong consequences. Therefore, suitable technologies must be used for treating this wastewater (Yassin, 2008). Rubber industries in Malaysia have implemented treatment facilities that consistent with regulations. Biological methods especially aerobic, anaerobic and facultative ponds are widely used for treatment of rubber wastewater in Malaysia (Usa, 2007). These systems are inexpensive and have a high efficiency for organic load reduction, but are appropriate for areas that land is available. Therefore, mechanical treatments such as anaerobic filter beds, rotating biodiscs and aerated lagoons are currently being used where land is limited (Chua and Garces, 1992; Kolmetz et al., 2003; Kantachote and Innuwat, 2004). As a result, the net organic

Table 3. Maximum standards for effluent discharge into wastewater for the rubber industry (Choo et al., 2003).

Parameter	Concentration (mg/l), 1984 and later
Biological oxygen demand	100
Chemical oxygen demand	400
Total solids	1000
Suspended solids	150
Ammonical nitrogen	300
Total nitrogen	300

Source: Environmental Protection Act 1996.

load of Malaysian's rubber effluents has been reduced by 80% in 1980-1985 (Chua and Garces, 1992; Daud, 2005). Most of rubber treatment plants now comply with the standards, but high pollutants concentration remains from rubber, because of improper discharges of a significant number of smallholdings and lack of adequate maintenance of their effluent treatment systems (Chua and Garces, 1992; Abdul Rani, 1995; Cleary and Chuan, 1999). In order to carryout organic pollution reduction, developing of improved purification systems for rubber effluents is essential (Guha, 1995). Also persistent attention and novel treatment methods will require for protection of Malaysia's rivers (Shirkie and Ching, 1983).

Another serious threat of rubber wastewater towards environmental protection is high concentration of nitrogen in this effluent. It contributes to undesirable eutrophication, economic loss, methemoglobinemia in infants, increases oxygen and chemical demands and affects the paddy field. Application of sulphuric acid in the coagulation of skim latex results in production of high level of sulphate in the effluent of rubber processing factories. The high levels of hydrogen sulphide (H_2S) will be liberated to the environment and cause malodour problems. The free H_2S also inhibits the digestion process, which gives lower organics removal efficiency. The odours are detectable even at extremely low concentrations and make water unpalatable for several hundred miles downstream from the rubber processing factories (Rungruang and Babel, 2008). Therefore, treatment of rubber wastewater using effective methods for overcoming to these problems is needed. Several processes have been developed for treatment of this wastewater in Malaysia. Several processes have been developed for treatment of this wastewater in Malaysia which will be discussed in details in this paper

CONVENTIONAL/CURRENT RUBBER WASTEWATER TREATMENT METHODS

Malaysian rubber wastewater treatment process was provided in 1995 (Lonholdt and Andersen, 2005). Various Wastewater treatment systems have been adopted by Malaysian rubber industry (Table 4). It has been found that the biological processes such as pond technology and aerobic and anaerobic methods are the most commonly used treatment systems. The existing biological method was also incorporated with sulphate reduction system and precipitation in order to further improve the efficiency of rubber wastewater treatment. Azolla and water hyacinth as a biological method and also deammoniation system are other alternative techniques that currently have been used for treatment of rubber effluent in Malaysia (Table 5).

BIOLOGICAL METHOD OF RUBBER WASTEWATER TREATMENT

Pond technology

Pond technology is a widely used method for treatment of effluents from the primary rubber industry in Malaysia. There are more than 500 palm oil and rubber factories in Malaysia which almost all have installed some type of primary wastewater treatment system like ponds (Usa, 2007). The pond systems usually include high loaded anaerobic ponds and low loaded aerobic ponds. Before the pond treatment system, there is a latex trap and a neutralization stage as a pretreatment step. If the ponds are effectively designed and optimally operated, it can remove over 95% biological oxygen demand (BOD) from rubber wastewater (Ahmad et al., 1980). Effluent with BOD levels of 50 - 100 mg/l can normally be achieved by methods mentioned above (Lonholdt and Andersen, 2005).

Moreover, pond technology is an alternative for rubber wastewater treatment in other countries like Thailand. Rakkoed and co-workers (1999) have used two kinds of waste treatment ponds (waste stabilization ponds and attached-growth waste stabilization ponds) as to compare the efficiency of nitrogen removal from concentrated latex wastewater. Working dimensions of each pond was 0.4 m^3 width, 1.2 m^3 depth and 0.6 m^3 length. During the first, second and last experiment run, hydraulic retention times (HRT) of 40 and 20 days, 40 days with 50% recirculating of effluent and 4 days was conducted. The results revealed that total Kjeldahl nitrogen (TKN), ammonia nitrogen (NH_3-N) and BOD_5 removal efficiencies in attached-growth waste stabilization ponds were higher than in control ponds. This is because of an increase in biomass on media in the pond water. In other hand, it has been reported that there is a treatment system in each co-operative

Table 4. Various rubber wastewater treatment systems and their efficiency

Treatment	Description	Initial COD (mg/L)	Initial BOD (mg/L)	Initial TKN (mg/L)	Initial sulphide (mg/L)	COD removal efficiency (%)	BOD removal efficiency (%)	TKN removal efficiency (%)	Sulphate removal efficiency (%)	SS removal efficiency (%)	Reference
Conventional/Current technologies											
Anaerobic filter.	Packed with aquarium media with dimension of 30 cm *100 cm; OLR = 11.8 gCODL^{-1} day^{-1} and HRT = 10 days.	18219	12750	-	-	92	-	-	-	-	Anotai et al. (2007)
Up-flow anaerobic sludge blanket (UASB).	Steel cylinder shape with dimension of 600 m^3 *250 m^3, consists of a waste water distributor, a lid for scraping sludge, dry rubber content and a gas-solids separator.	6100	-	315	-	80	-	80	90	-	Taechapatarakul (2008)
Biological method incorporated with sulphate reduction system (purple non-sulphur photosynthetic bacteria).	Optimum growth in latex rubber sheet wastewater with 0.50% ammonium sulphate and 1 mg/l nicotinic acid in a pure culture and or a mixed culture.	7328	4967	-	-	90	90	-	92 - 96	-	Kantachote et al. (2005)

operative rubber sheet factories in Thailand that it is minimally maintained, and not being functioned based on the design. Actually, there are two models of the treatment systems that consist of four ponds with different sizes according to the available land of factory. Due to high maintenance and energy costs of surface aerator, all of these factories had stopped using it. This makes to low quality of the effluent from these systems which unable to meet the industrial effluent standards in Thailand (Chaiprapat and Sdoodee, 2007). A series of ponds were also used for treatment of 4.58 m^3/ton of wastewater from smoked sheet rubber factories in southeast Thailand. In this study, HRT 90-120 days were used for reducing the nitrogen of rubber wastewater. The results showed that the number and size of ponds were not adequate for treatment of wastewater. Therefore, it caused to serious water pollution and unpleasant odour to the neighbouring villagers (Puetpaiboon et al., 2005; Taechapatarakul, 2008). In general, settling ponds have few drawbacks which it takes sixty days. That means a great amount of water has to be kept over time for treatment. This method needs a large area of land, operating cost and time (Clay, 2004; Shamsudin et al., 2006).

Aerobic and anaerobic treatment

Biological treatment of rubber wastewater is a method, which gives the greatest reduction of BOD (Rungruang and Babel, 2008). Aerobic and anaerobic treatment is the most common biological method used in Malaysia for treating rubber wastewater as it is an inexpensive treatment with high efficiency (Kolmetz et al., 2003; Kantachote and Innuwat, 2004). In some rubber factories where land area is limited, aeration systems are used as an alternative of settling ponds. Conventional treatment systems

Table 4. Continued.

Treatment	Description	Initial COD (mg/L)	Initial BOD (mg/L)	Initial TKN (mg/L)	Initial sulphide (mg/L)	COD removal efficiency (%)	BOD removal efficiency (%)	TKN removal efficiency (%)	Sulphate removal efficiency (%)	SS removal efficiency (%)	reference
Advanced technologies											
Natural process.	Consists of VF followed by SSF with nut grass (*Cyperus rotundus* Linn) plantation.	5750 - 18303	780 - 9625	102 - 157.6	85 - 460	99	99	97.8	93.6	-	Puetpaiboon et al. (2005)
Electrochemical methods.	Electrolytic reactor, anode and catode with dimension of 300*, 450, 270*, 60, 270 and *50 mm; thickness = 0.8 mm and electrolysis period = 90 min.	2000 - 6000	1000 - 3500	250 - 700	250 - 400	99.9	98.8	-	-	-	(Vijayaraghavan et al., 2008a)
Ozonation followed by batch activated sludge process.	ozone dosage = 66.44 mg O_3/ L O_2 of; pH = 9.0 and contact time = 30 min.	999 - 1160	350 - 398	165 - 199	1642 - 2045	91.49	95.79	67.95	74.68	-	Rungruang and Babel (2008)
Combined physical, chemical and biological methods (gas injection technique).	-	-	-	-	-	67	77	51	95	-	(Yusoff et al., 2004)

are well set up using aeration systems with sludge recycling to increase the microbial concentrations in the aeration tanks (Shamsudin et al., 2006). It can remove over 95% of BOD from the rubber wastewater (Ahmad et al., 1980). This system can overcome malodour and are suitable for factories with inadequate land area. However, the existing system was not effective in removing nitrogen because of an insufficient supply of dissolved oxygen for nitrification (Nordin, 1990).

In 1971, the Rubber Research Institute of Malaysia (RRIM) used the biological processes for the treatment of rubber factory effluent. This system consists of improved anaerobic and aerobic processes. Coconut fibre as a new medium was selected for rubber wastes treatment. The availability, high specific surface area, high water holding capacity and a balanced C/N/P ratio of coconut fibre are favourable characteristics for biofiltration applications (Karim and Vaishya, 1999; Suwardin et al., 1999; Gabriel et al., 2007). Since, waste oil palm fibres have a shorter retention time and narrower space; it is also possible to get the high efficiency in wastewater treatment using these media (Suwardin et al., 1999).

Several types of enclosed anaerobic digesters have also been evaluated for treatment of rubber effluent in lab scale. Hollow cylindrical clay, polyurethane foam and rubberised coir were chosen as a packing material in these digesters (Ahmad, 1983; Zaid, 1988, 1992) for attaching the microbial growth in anaerobic filter as a packed bed reactor, used form of inert static medium. It

Table 5. Other rubber wastewater treatment methods.

Treatment method	Description	Result	Reference
Azolla as a biological treatment.	Using the tiny floating fern *Azolla* for treating of wastewater from sugar refineries and rubber processing plants in Malaysia.	Extraction of compounds containing nitrogen.	MacKinnon et al. (1996).
Water hyacinth as a biological treatment.	Plants such as water hyacinth used for treatment of Malaysian rubber sewage and recovery of dissolved nutrients.	A reduction of 99 and 80% in BOD and COD. Decline the suspended solids of treated wastewater to the less than 50 mg/l using combined system. More efficiency of combined algae-water hyacinth system for removal of nitrogen as compared to the normal high rate algal pond.	Kulatillake and Yapa (1986); Gamage and Yapa (2001); Bich et al. (1999) .
Deammoniation system.	Removal of ammonia from skim latex using a slatted-plate system and a new deammoniation system, known as POTORRIM that was developed by RRIM.	Overcoming to some problems encountered with slatted-plate system provides more efficient deammonification and effective cleaning using POTORRIM.	Nordin (1993).

was revealed that the filter can accept loadings of up to 8 kg COD/m^3/day. The results also showed that only 50% of chemical oxygen demand (COD) was removed that could possibility be due to packing used (Ahmad, 1983). At the same loading rate, higher COD removal (70%) was achieved with polyurethane foam and hollow cylindrical clay (Zaid, 1988). Moreover, clogging may be a main problem with these packed bed systems and the influents need to be filtered prior to treatment. This problem has led to the development of anaerobic sludge blanket reactor (UASB) (Ahmad et al., 1986).

Taechapatarakul (2008) used UASB reactor which is in a steel cylinder shape with the dimensions of 600 and 250 m^3. It worked 8-24 h a day and consists of a wastewater distributor, a lid for scraping sludge, dry rubber content and also a gas-solids separator. It has been found that the UASB are able to carryout agglomeration of granular sludge forming a stable blanket in the reactor. Fast breakdown of organic materials can be achieved due to the ability of granular sludge for retention of high solids in the reactor. UASB system is a close system that can control the fault smells which comes from applied oxidation and stabilization ponds. Moreover, this system consumes low electricity energy that can help saving a lot of money. The main problem of the UASB is difficulty in developing the granular sludge blanket and maintaining its stability. However, this system was used in many industries but it still never approved that it could work appropriately with natural rubber wastewater (Taechapatarakul, 2008).

Combined aerobic and anaerobic digestion has been used for biogas production from rubber wastewater in Batang Kali, Selangor, Malaysia. This plant produced about 8000 m^3 of biogas per day that will be used as a fuel in the boilers for the production of steam. These technologies are commercialised in the Philippines, Hong Kong and Singapore (http://www.cogen3.net/fsdp-rubber malay.html). Moreover, the 32 manufacturing plants in Thailand produced 254 million m^3 per year of methane from solid waste and wastewater (Priwan, 2008).

On the other hand, aerobic and anaerobic treatment methods are not acceptable by government and industry due to problems about control of microoganisms such as introduction of unknown foreign species, genetic mutation, insufficient scientific evidence, high cost of technology and others (Tan, 2007).

BIOLOGICAL METHOD INCORPORATED WITH SULPHATE REDUCTION SYSTEM

Low cost operation, high removal efficiency and also producing the biogas as a useful energy sources are some advantages of anaerobic wastewater treatment system (Kantachote et al., 2008). However, this treatment results in the formation of H_2S due to consumption of sulphate instead of oxygen by sulphate-reducing bacteria. H_2S is toxic and increases the smell of putrid eggs. The gas also causes a big problem in biogas producing systems (Kantachote and Innuwat, 2004). As a result, sulphide could inhibit the activity of methane producing bacteria due to its toxicity. It also revealed that the high amount of sulphide reduced the COD removal. Therefore sulphide elimination is an important stage for this kind of wastewater before a biogas production step (Kantachote et al., 2008).

Sulphate reduction reactor (SRR) has been used for treatment of sulphate rich rubber wastewater from concentrated latex and skim crape. The SRR is needed for reduction of sulphate concentration in wastewater before biogas production by UASB. However, the produced biogas does not have a good quality due to its high amount of H_2S. Therefore, the biogas was burnt to remove the very toxic and corrosive H_2S gas.

Hence, converting the sulphide to sulphur by partial oxidation is needed. It is realized that levels of sulphide oxidation are dependent on oxygen concentration. Additionally, bacteria with ability of oxidizing reduced sulphur compounds can be used for removal of H_2S from treated wastewater or gaseous systems. Thus, selection of a microbe that can grow at room temperatures and neutral pH with ability of oxidizing sulphide to sulphur in wastewater is important (Taechapatarakul, 2008; Kantachote et al., 2008).

Identification of bacteria which can grow in the concentrated latex wastewater was studied by Choorit et al. (2003). In this work, the efficiency of the isolated strains for organic content reducing of concentrated latex effluent was evaluated. The purple non-sulphur photosynthetic bacteria which were isolated from a concentrated latex effluent were cultured in a wastewater without any supplementation. After 40 h of cultivation, 34% of COD was decreased by *Rubrivivax gelatinosus* and *Thiobacillus* sp. (Choorit et al., 2003).

Thiobacillus sp. meanwhile is extensively used worldwide for removal of both organic and inorganic sulphur compounds in wastewater. *Thiobacillus* sp. can reduce inorganic sulphur compounds as an energy source and therefore is used for removing sulphide from wastewater. Four kinds of *Thiobacillus* sp. were isolated from domestic and rubber wastewaters in Thailand by Kantachote and Innuwat (2004). All isolates could grow in pH of 2.0 - 7.0 (optimum 6.5), temperature of 25 - 45℃ (optimum 30 - 35℃) under both aerobic and anaerobic conditions. The results showed that the highest COD removal (54%) can be obtained by *Thiobacillus* sp. WI1 which cultivated in rubber sheet wastewater for 14 days. However, it does not show the good ability for BOD reduction and it declined by only 33%. Against, the efficiency of strain WI4 for BOD and COD removal was 83 and 46% (Kantachote and Innuwat, 2004).

Kantachote et al. (2005) also isolated some purple non-sulphur photosynthetic bacteria (PNSB) from rubber sheet wastewater in Thailand. Isolate DK6 as a kind of *Rhodopseudomonas* shows the best potential for effluent treatment since it can grow well under microaerobic-light conditions and a mixed culture. It has been found that the mixture of 0.50% ammonium sulphate and 1mg/l nicotinic acid with latex rubber sheet wastewater makes the optimum growth of DK6. Using these conditions and either under a pure or a mixed culture, it can reduce the COD and BOD of wastewater to 90%.

Therefore, it can be concluded that using the bacteria strains for rubber wastewater treatment is an environmental friendly method and ecologically balanced. This technology is also applicable in other organic waste disposal and has good potential in Malaysia and other Asian countries (Kamaruddin, 2007).

BIOLOGICAL METHOD INCORPORATED WITH PRECIPITATION

One of the parameter that can affect the efficiency of biological treatment processes is the presence of heavy metals such as zinc in wastewater. Adsorption, membrane separation and precipitation are some examples of effective technologies that have been used for removal of heavy metals from wastewater (Agamuthu, 2004; Wright and Nebel, 2007). Currently, simple and inexpensive method such as precipitation by hydroxide is the more common approach that are used in Malaysia. However, this method is not suitable for highly organic polluted rubber wastewater due to zinc-organic ligand complexes production. Therefore, reduction of organic matter that includes heavy metals from wastewater is required. It has been found that some kinds of microorganisms in anaerobic and aerobic processes can be used for this purpose. Microbial flocculation under aerobic conditions can be avoided by high amount of total dissolved solids (TDS) in rubber wastewater. In order to meet the effluent standards, rubber factory have to use some tertiary treatment such as coagulation and filtration processes to remove the excess solids. This significantly increases their treatment and disposal costs. Therefore, reduction of the TDS to a level that does not inhibit or interfere with aerobic microbial aggregation is required. Another method for removal of heavy metal is sulphide precipitation.

In this process, use neutral pH which is also suitable for microbial growth (Eckenfelder, 1999). In addition to, the removal efficiency of sulphide precipitation is usually better than the hydroxide treatment under a low dissolved solid condition. Therefore, sulphide precipitation is a more promising option than the recent technology. In other hand, adjustment of optimal dosage in hydroxide precipitation system is much easier than sulphide method especially under frequent fluctuation of zinc concentration. In fact, high amount of sulphide can makes malodour and also excessive residual sulphide whilst inadequate dose of precipitant can results in an effluent with high amount of zinc. Therefore, study about the effect of important parameters on sulphide addition control system which is easy and cheap are needed. Chemical and biological processes without any pH adjustment were used for treatment of acidic latex wastewater with high amount of zinc. Sulphide and hydroxide precipitation increased the total dissolved solids of treated effluent by 1.1 and 2.8 times, respectively.

92% of TDS was removed by anaerobic filter in more than 11.8 gCODL^{-1} day^{-1} of organic loading rate. For the activated sludge process, average removal efficiencies for COD and BOD were 96.6 and 99.4%. This combined system was verified to be an effective method for purification of rubber thread wastewater (Anotai et al., 2007).

Another most cost effective system for zinc removal from the wastewater in Malaysia is using a mixture of 800 mg/l of sodium sulphide and 5 mg/l of polyelectrolyte LT27, respectively. The optimum settling time and flocculation time were 60 and 20 min. The best results can be obtained in a speed of 20 rpm in a 110 mm diameter reactor. The approximate cost of this system is RM1.04/m^3 (US $0.26/m^3) of wastewater discharged (Subbiah et al., 2004).

In a study by Kolmetz et al. (2003), the efficiency of an expanded bed biofilm reactor in the treatment of wastewaters contaminated with heavy metals has been investigated for rubber product manufacturing industry. Some advantages of biofilm systems are ability to retain relatively high biomass concentrations that results in shorter liquid retention times, better performance stability and higher volumetric removal rates. In the study, it has been found that the process could achieve 60 to 90% removal of Zinc. In addition, the efficiencies of an expanded bed biofilm reactor and a sequencing batch biofilm reactor for heavy metal adsorption were studied using Zn and Cu containing wastewaters. The results showed that heavy metal adsorption by these reactors are 50 - 95% (Mohamad, 2007).

ADVANCED RUBBER WASTEWATER TREATMENT METHODS

Currently, several effective methods have been used for treatment of rubber wastewater in Thailand which makes natural rubber industry more environmentally friendly and economically viable. In response to problems associated with rubber wastewater and its effect on the Malaysian's environment, further research can be performed to develop the novel methods for treatment of this wastewater. As follow some inventive technologies that were used in Thailand and Malaysia will be described. The best novel methods also are shown in Table 4.

Natural process

A constructed wetland is an artificial marsh or swamp that includes substrate, vegetation and biological organisms contained within a physical configuration. Suitability designed and operated wetlands have considerable potential for low-cost, efficient and self maintaining wastewater treatment systems. This system has demonstrated capability to remove nutrients, suspended solids, organic compounds, pathogens and metallic ions and to increase oxygen and pH levels in wastewater. In comparison to conventional systems, lagoons or land application flow, wetlands waste treatment systems require fewer amounts of capital and operating costs, minimal operator training and land area (Hammer, 1989).

Puetpaiboon et al. (2005) studied the possibility of treat wastewater from a rubber sheet factory in Thailand using the pilot-scale experiment constructed wetland (CW). This system consisted of vertical flow constructed wetlands (VF) followed by subsurface flow constructed wetlands (SSF) with nut grass (*Cyperus rotundus* Linn.) plantation. The tested COD loadings in this experiment were 500, 750, 1000 and 1250 kg COD/ha.d. The results showed that the best removal efficiency of BOD5, COD, SS and TKN were 99, 99, 93.6 and 97.8%, respectively, using VF followed by SSF with nut grass (*C. rotundus* Linn.) plantation at 750 kg COD/ha.d.

Biological method

One of the extensively used methods for removal of dissolved and colloidal organics in wastewater is the activated sludge process. This system changes the dissolved and colloidal organic contaminants to a biological sludge which can be removed by settling. After a primary settling basin, usually use an activated sludge process as a secondary treatment (Cheremisinoff, 1998).

Chevakidagarn and Ratanachai (2004) and Chevakidagarn (2006) surveyed two rubber treatment plants, which are single-stage activated sludge process in Songkhla, Thailand. They reported that the suspended solids removal capacities were low (from 78 to 87%). The treatment plants often had bulking and rising sludge problems because of insufficient oxygen concentrations. Thus, it is recommended that an appropriate oxygen control system to be included in this system for the rubber industry to ensure sufficient oxygen is provided. This will assist in compliance with the effluent standards.

Chevakidagarn et al. (2006) also upgraded the operation of conventional activated sludge treatment plants to save aeration energy and at the same time to provide better utilization of existing plant capacity for nutrient removal without major financial investment. The first stage of the experiments was to observe the possibility of using oxidation-reduction potential (ORP) for aeration control in treatment plant fed with the wastewater from the latex rubber industry. The results proved that the ORP was greatly affected by the change in air supply. However, it was also affected by the fluctuation of wastewater temperature, which contributed to the bulking sludge problem.

In another study, Chevakidagarn (2005) used surrogate parameters for rapid monitoring of contaminant removed for activated sludge treatment plant for rubber and seafood industries in Southern Thailand. UV absorbency at various wavelengths was used in this study as surrogate parameters, for predicting the removal capacity of each plant. The results showed that UV absorbency at 220 nm can be used as a parameter to predict nitrate-nitrogen concentrations which less than 15 mg/l. Also, it was found that 550 and 260 nm are suitable wavelengths for predicting of suspended solids concentration and COD.

In generally, aerated lagoon or activated sludge can reduce fault smell of rubber wastewater but have a high consumption of electricity and relatively high investment and operation costs (Puetpaiboon et al., 2005; Taechapatarakul, 2008).

Chemical methods

Electrochemical methods: Longer hydraulic retention time is needed for treatment of rubber wastewater by conventional biological methods and sometimes exposure to failures if shock loaded. Recently, much more attention has been drawn to electrochemical method for treatment of wastewater due to the cost, ease of control and the increased efficiencies provided by the use of new electrode material and compact biopolar electrochemical reactor (Sequeira, 1994; Rajeshwar and Ibanez, 1997; Vijayaraghavan et al., 2008b). The electrochemical treatment methods are preferred as the less required of hydraulic retention time.These systems are not successful because of variation in wastewater strength or due to the existence of toxic material. Generation of chlorine or hypochlorous acid is the best alternative method for performing the electrolytic treatment. Therefore, there is a considerable interest for developing a new method of wastewater treatment based on *in situ* hypochlorous acid generation as a kind of electrochemical method (Vijayaraghavan et al., 2008a, b). An electrolytic cell including of graphite as anode and stainless sheets as cathode was providing the hypochlorous acid. For organic destruction of the rubber wastewater used, the produced hypochlorous acid acts as an oxidizing agent. The results showed the efficiency of 99.9 and 98.8% for COD and BOD removal. Moreover, it has been indicated that pH 7.3; TOC 45 mg/l; residual total chlorine 136 mg/l; turbidity 17 NTU and temperature 54EC can be obtained by this system for an influent with the initial pH 4.5; current density of 74.5mA/cm^2; sodium chloride content 3% and electrolysis period of 90 min, respectively. At the same condition and up to 2% of sodium chloride concentration, 95.7 and 88.6% of COD and BOD removal, pH 7; TOC 90 mg/l; residual total chlorine 122 mg/l; turbidity 26 NTU and temperature 60EC can be achieved (Vijayaraghavan et al., 2008a).

Ozonation

Some of the non-biodegradable materials and also ammonia nitrogen of natural rubber wastewater cannot be completely removed using biological process. Therefore, the organic contents of effluent are above those of the standard limits. It is generally approved that ozonation transforms refractory or poorly degradable organic materials into by-product with smaller molecular size. Moreover, it has been found that ammonia can be converted to nitrate by ozonation which usually makes biodegradability.

Rungruang and Babel (2008) studied the efficiency of batch activated sludge process (BAS) with or without ozonation for rubber wastewater treatment at Chonburi, Thailand. The effects of different contact times (0 - 90 min) and ozone dosages (37.20, 56.90 and 66.44 mg O_3/ L O_2) at various pH (7.4, 9.0 and 11.0) on wastewater treatment were studied. As a result, it was found that 66.44 mg O_3/ L O_2 of ozone dosage; pH of 9.0 and 30 min of contact time are the optimum conditions for reduction of pollutants. It has been found that the combination of BAS and ozonation makes higher removal efficiency for all parameters compared to another system (Rungruang and Babel, 2008; Spellman, 2003; Qasim, 1998).

Combined physical, chemical and biological methods

The combined processes were found to be very effective in treatment of rubber wastewater in Malaysia and Thailand. Iyagba et al. (2008) reported that for removing the high levels of ammonia nitrogen from anticoagulants which is used in treating raw rubber of Asia-Pacific Region, aeration alone systems is not efficient. Combined physical and chemical treatment systems followed by two-stage biological method was used for fibre and suspended solids removal in Malaysia. This work involved the installation of a fibre screening system, a dissolved air flotation system, an aeration basin, a secondary clarifier and a sludge dewatering system. This process could produce an effluent which is consistent with the DOE Standard A (Kolmetz et al., 2003).

Application of membrane technology that involves gas injection technique is another alternative for treatment of natural rubber effluent in Malaysia. The results showed that total permeate flux was enhanced from 8.3 to145.3% using gas sparging technique. In terms of permeate quality, 95, 67, 77, 51, and 74%, of reductions were achieved for total solids, COD, BOD, total nitrogen and NH_3-N, respectively. For the non-gas sparging system, permeate flux declined sharply with time due to the accumulation of foulant on the membrane surface. However, both conditions showed increase of total permeate flux with transmembrane pressure and feed flowrate (Yusoff et al., 2004).

55 concentrated latex factories exist in southeast Thailand which also used combination of physical and biological methods for treatment of wastewater. Trapping of rubber as a physical process was used for removal of suspended rubber. The biological treatment that was utilized in 22 factories was

stabilization pond which includes anaerobic, facultative and aeration ponds. Anaerobic ponds with aerated lagoon were installed in 24 factories and in the 5 of them, activated carbon processes were utilized. UASB and land application were another methods that used by 1 and 3 factories. All of these technologies were not suitable for reduction of COD, BOD, magnesium and sulphate from concentrated latex wastewater but are capable for hardly removing nitrogen and phosphorous (Furumai et al., 2007).

CONCLUSION

Recently, several processes have been used for treatment of rubber wastewater in Malaysia. Advantages and disadvantages of these methods rely on simplicity, flexibility and effectiveness of the operation, cost, technical problems and maintenance. Therefore, more economical alternative technologies for the treatment of wastewater from rubber factories are required. Conventional treatment options have been favoured in the past for treatment of rubber effluent but biological treatment especially aerobic, anaerobic and facultative ponds are becoming increasingly popular since they are inexpensive and have a high performance for organic load reduction. Moreover, novel systems for management of agro-industrial wastes have been developed to overcome the problems of conventional systems. However, these advanced methods should be calibrated based on rubber effluent characteristics in Malaysia and, at the same time, the efficiency of these methods has to be improved. Generally, production of good effluent quality from rubber wastewater treatment can be accelerated by these innovative techniques.

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