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COMPARISON OF COD AND TSS REMOVALS FROM ARTIFICIAL RIVER WATER BY MUDBALLS MADE WITH ACTIVATED EM1 AND EM4 SOLUTIONS

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ABSTRACT: In Indonesia, surface waters are often polluted by domestic waste. The use of Effective Microorganisms (EM) mixed with rice bran and clay soil then shaped into mudballs has been suggested as a means to directly improve water quality of polluted rivers. This study examined the removal of COD and TSS by 2.5 cm ϕ mudballs made with two different kinds of activated EM solutions, i.e. EM1 and EM4. Batch experiments at 30°C were conducted where artificial river water was treated with mudballs made from rice bran, and clay soil, which was mixed with either activated EM1 or EM4 solutions. Removal efficiencies of 120 mg/L COD by the mudballs were respectively 60.3% with EM1 and 59.4% with EM4. Removal efficiencies of 100 mg/L TSS were respectively 100% with EM1 and 97.9% with EM4. Statistical hypothetical testing of the experimental data suggests that at α=0.05, there is no difference in removal efficiencies of COD and TSS by mudballs made with either EM1 or EM4. COD and TSS removal efficiencies are correlated with mudballs' diameter; where increasing diameter results in better removal efficiencies. pH values of artificial river water after 5 days treatment by mudballs mixed with EM1 and EM4 were respectively 6.2 and 4.8. TSS isotherm sorption by mudballs with EM1 better fits the BET model, with q_m= 32.4 mg/g, whereas that with EM4 better fits the Langmuir model, with Q_m = 7.52 mg/g; K_L = 0.0168 L/mg and R_L = 0.373. It appears that EM1 would be the preferred EM solution for direct treatment of polluted surface waters.

Keywords: Adsorption isotherms, Effective Microorganisms, Mudballs, River Water

1. INTRODUCTION

Urban rivers are major assets to communities as they provide numerous benefits, including fresh water, recreation, landscape amenity, habitat provision and flood control [1]. However, in Indonesia, surface waters are often polluted by both domestic as well as industrial waste. For instance, the average COD and TSS levels of Cikapundung River, Bandung City, Indonesia in 2013 were 120 mg/L and 100 mg/L respectively; with maximum levels at times reaching as high as 400 mg/L COD and 350 mg/L TSS [2].

Although conventional physical-biological treatment methods can be applied to treat polluted surface waters, they are often costly and not eco-friendly. Hence the use of Effective Microorganisms (EM) that are mixed with clay soil and shaped into balls, - known as "EM mudballs", - has been proposed as an alternative means to directly improve the water quality of polluted rivers [3]. These so-called "EM-mudballs" are capable of reducing suspended solids, turbidity, as well as COD content of the polluted river; which would also improve the river's DO content.

The concept of EM, which is a mixed culture of naturally occurring effective, beneficial, non-pathogenic microorganisms was first promulgated by Professor Dr. Teruo Higa of the University of Ryukus, Okinawa, Japan and have been applied for amongst others the treatment of water and wastewater, improvement of recycled water and solving sanitary problems [4].

Nugroho et al. [2] reported that the removal efficiencies of 120 mg/L COD and 100 mg/L TSS from artificial river water by 2.5 cm ϕ mudballs made from rice bran, clay soil and EM4 activated solution at 30°C were 59.4% COD and 99.7% TSS respectively.

However, the pH of artificial river water treated by EM4 mudballs becomes acidic even when the pH value of the artificial river water solution was initially alkaline [5]. pH values in the acidic range could potentially harm aquatic organisms, and in fact, based on statutory Indonesian regulations, pH of Indonesian surface waterways must range between 6-9. EM4 is manufactured locally in Indonesia, and consists of a mixed culture of Gram-negative and Gram-positive rod-shaped bacteria, some of which are spore-forming, as well as *Mucor sp.* and *Penicillium sp.* fungi, and actinomycetes [5].

In Malaysia, mudballs made from EM1 activated solution (EMS) have been used to clean up rivers, including Sungai Kelian in the state of Perak where EM-mudballs improved river water quality from Class IV (suitable for irrigation) to Class III (suitable for water supply with extensive treatment) [3]. EM1 is the original Effective Microorganisms solution developed by Dr. Higa in the 1980s, made up of a mixed culture of microorganisms including lactic acid bacteria, photosynthetic bacteria, actinomycetes, yeasts, and fermenting fungi.

As artificial river water treated with EM4 mudballs produces an acidic pH value [5], the objective of this current study was, therefore, to discern whether EM1 mudballs also produce similar results. The removal efficiencies of COD and TSS in artificial river water by mudballs made with either EM1 or EM4 solutions were therefore compared. Parameters analyzed included COD and TSS removal efficiencies, change in pH values of the treated artificial river water, the correlation between removal efficiencies and mudballs' diameter as well as TSS isotherm adsorption model.

2. METHODS

All experiments were conducted as batch experiments. COD was measured by close reflux titrimetry, TSS was measured by gravimetry methods and pH was measured using Lutron pH-208 pH-meter.

2.1 Materials

The EM1 solution used in the experiments is a registered trademark of EMRO and was procured from Seikatsu, Japan. Whereas, the EM4 solution used in the experiments was manufactured by Songgo Langit Persada and procured locally in Bandung, Indonesia. The EM solutions are sold in a dormant state and hence had to be activated. Activation of the dormant EM solutions was performed by diluting 5% EM solution with distilled water and leaving the mixture to ferment for a day at room temperature [5].

The mudballs (MB) were prepared by mixing 20% rice bran and 80% dry clay soil with 40% activated EM solutions (v/w), shaped into 2.5 cm ϕ balls, which were then left to ferment in covered baskets for 7 days at room temperature.

Artificial river water with a COD content of 120 mg/L and TSS content of 100 mg/L was prepared by adding glucose and 60 mesh sieved kaolin powder into tap water [5].

2.2 Experiments

2.2.1 Batch experiments with artificial river water

The batch experiments were carried out in 250 mL Erlenmeyer flasks. Mudballs (MB) made with either EM1 (EM1-MB) or EM4 (EM4-MB) activated solutions were mixed with 200 mL artificial river water. The flasks were then incubated in a shaker water bath at 30°C. The COD, TSS and pH values of the treated river water solutions were measured daily.

2.2.2 TSS adsorption experiments

The TSS adsorption experiments were carried out in 250 ml Erlenmeyer flasks containing 200 ml tap water mixed with kaolin powder producing a TSS concentration of 100 mg/L. Varying quantities of EM1-MB or EM4-MB (1 - 10 g) were then added to the TSS solution and the flasks placed in a shaker water bath adjusted to 30°C. The TSS was measured after 3 days of shaking.

2.2.3 Calculation of adsorption isotherms

Adsorption isotherms describe the equilibrium relationships between adsorbent and adsorbate [6]. The isotherm equations used to determine the TSS adsorption model were the Freundlich, Langmuir, and Brunauer-Emmett-Teller (BET) isotherm equations. The Freundlich isotherm is an exponential equation that assumes that as the adsorbate concentration increases so too does the concentration of the adsorbate on the adsorbent surface [7]. This isotherm can be used for non-ideal sorption that involves heterogeneous surface energy systems, hence not restricted to the formation of a monolayer. The mathematical expression of the Freundlich isotherm is as follows:

$$\frac{X}{M} = K_F C_e^{\frac{1}{n}} \tag{1}$$

Where $\frac{X}{M}$ is the amount of adsorbate adsorbed by the adsorbent (mg/g), K_F is a rough indicator of the adsorption capacity (mg/g), 1/n is the adsorption intensity and C_e is the equilibrium liquid-phase concentration of the adsorbate (mg/L).

The Langmuir isotherm equation is based on the assumption of monolayer coverage (the layer is one molecule thick) of adsorbate over a homogenous adsorbent and that when equilibrium is attained no further adsorption can take place. Adsorption is assumed to take place at specific homogenous sites in the adsorbent and the adsorption of each molecule has equal adsorption energy [8]. The theoretical Langmuir isotherm equation is as follows:

$$\frac{X}{M} = \frac{Q_m K_L C_e}{1+K_L C_e} \tag{2}$$

where Q_m is the maximum amount of adsorption corresponding to complete monolayer coverage on the surface (mg/g); and K_L is the Langmuir constant related to the energy of adsorption (L/mg).

The Brunauer-Emmett-Teller (BET) adsorption isotherm is a theoretical equation that was developed in order to describe multilayer adsorption systems [9]. The model assumes that a number of layers of adsorbate accumulate at the surface and each layer follows the Langmuir isotherm model. As such, the BET isotherm equation is as follows:

$$\frac{q}{q_m} = \frac{bc}{(C_s-1)[1+(b-1)C/C_s]} \quad (3)$$

where C is the aqueous concentration of adsorbate (mg/L), C_s is the saturation concentrations for adsorbate in solution and q_m is the maximum capacity of adsorbent for adsorbate (mg/g).

3. RESULTS AND DISCUSSIONS

3.1 COD and TSS Removal Efficiency

Figure 1 shows the results obtained regarding COD and TSS removal efficiencies by 2.5 cm ϕ MB made with either EM1 or EM4 activated solutions (EM1-MB and EM4-MB). Whereas, Table 1 shows the changes in pH, COD, and TSS values over time in artificial river water treated with EM1-MB and EM4-MB.

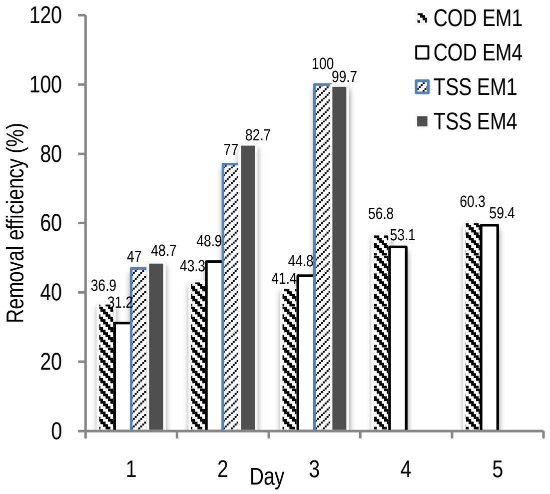

Fig. 1 COD and TSS removal efficiencies (%) of artificial river water EM1-MB and EM4-MB at 30°C

The results presented in both Fig. 1 and Table 1 show that maximum COD and TSS removals were attained after 5 and 3 days incubation respectively at 30°C. COD removal efficiencies by EM1-MB and EM4-MB were respectively 60.3% and 59.4%; hence it initially appeared that slightly better COD removal was obtained with EM1-MB. Likewise, slightly better TSS removal efficiency was obtained with EM1-MB as TSS removal efficiency with EM1-MB was 100%, while that of EM4-MB was 99.7%. Accordingly, to confirm whether COD and TSS removal efficiencies by EM1-MB and EM4-MB are different, statistical hypothetical testing against the COD and TSS experimental data was performed. The results are presented in Table 2.

Table 1 Changes in pH, COD and TSS values of artificial river water treated with EM1-MB and EM4-MB at 30° C

Day	pH		COD (mg/L)		TSS (mg/L)	
	EM1	EM4	EM1	EM4	EM1	EM4
0	5.1	4.1	120	120	100	100
1	5.5	4.65	75.7	82.6	53.3	51.3
2	5.5	4.48	68.1	61.3	22.3	17.3
3	5.7	4.6	70.3	66.2	0	0.67
4	6	4.76	51.9	56.3	0	0.67
5	6.2	4.82	47.6	48.7		
6	6.2	4.82	47.6	48.7		

Table 2 Statistical hypothetical testing of COD and TSS removal efficiencies by EM1 and EM4 Mudballs

	% COD removal	% TSS removal
α	0.05	0.05
Hypothesis	$H_0 : \mu_{EM1}=\mu_{EM4}$ $H_1 : \mu_{EM1}>\mu_{EM4}$	$H_0 : \mu_{EM1}=\mu_{EM4}$ $H_1 : \mu_{EM1}>\mu_{EM4}$
Results of t testing	$t_{calculated} < t_{table}$	$t_{calculated} < t_{table}$
Conclusion	% COD removal by EM_1= % COD removal by EM_4	% TSS removal by EM_1 = % TSS removal by EM_4

The results presented in Table 2 show that at α=0.05, COD and TSS removal efficiencies by mudballs made with either EM1 or EM4 activated solutions are the same. COD removal is attributed to both physical (sorption) and biodegradation processes, whereas TSS removal is attributed to physico-sorption processes alone [2].

With regard to changes in pH values (Table 1), after 5 days the pH value of artificial river water treated with EM4-MB was pH<5, whereas that treated with EM1-MB was pH>6. Accordingly, the pH of artificial river water treated with EM1-MB meets Indonesian statutory regulations, while that treated with EM4-MB does not meet statutory Indonesian regulations. The differences in pH values are attributed to differences in the types of microorganisms present in EM1-MB and EM4-

MB. EM4 solution includes mixed cultures of Gram-negative and Gram-positive rod-shaped bacteria, some of which are spore-forming, as well as actinomycetes and fungi of the *Mucor* and *Penicillium* genera [5], whilst the EM1 used in this study contains amongst others *Bacillus sp*. as well as Gram-negative rod shaped non-spore forming bacteria, as well as fungi such as *Mucor sp*.and *Bipoloris sp.* [10]. Both *Bacillus sp.* and Gram negative rod-shaped non-spore forming bacteria are not categorized as lactic acid bacteria given that by definition lactic acid bacteria are Gram-positive, non-sporeforming cocci, coccobacilli or rods that ferment glucose to lactic acid or to lactic acid, CO_2 and ethanol. Therefore different types of microbial consortia present in the EM solutions would attribute to differences in the abilities of the EM1 and EM4 microorganisms to produce organic acids that in turn would affect the pH values. In comparison, Namsivayam et al. [11] reported that after 5 days domestic sewage treated with EM solution composed of *Lactobacillus planetarium* (lactic acid bacteria), *Candida utilis* (yeast), *Streptomyces albus* (actinomycetes) and *Aspergillus oryzae* (fungi) had a pH of 8.4 and 14% reduction in COD. The SS, DO, COD, BOD and pH values of Kelian River, Malaysia improved after being treated with mudballs made from EM1 activated solution [3]. On the other hand, after 12 days of incubation at room temperature the pH of produced water treated with EM solution composed of *Lactobacillus plantarum*, *Aspergillus sp.* and *Penicillium italicum* decreased from 8.03 to 3.71 and had a COD reduction of 60% [12].

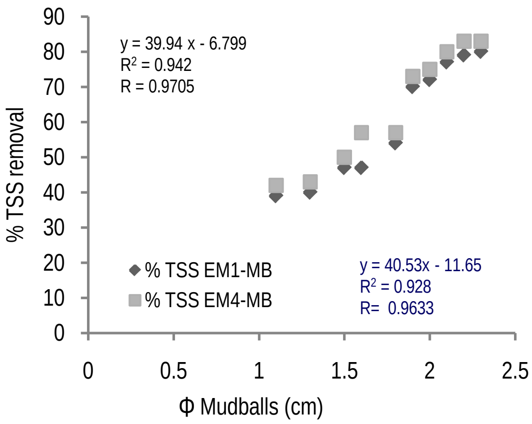

Fig. 2 Correlation between TSS removal efficiency and mudballs' diameter

Figures 2 and 3 respectively depict the correlation between removal efficiencies of TSS and COD with mudballs' diameter. As shown in Fig. 2 and Fig. 3 the determination coefficient (R^2) and the correlation coefficient (R) indicate a high correlation between TSS as well as COD removal efficiencies against mudballs' diameter, whether this is with EM1 or EM4. The correlation coefficient (R) for TSS removal efficiency against mudball diameter is 0.9633 and 0.9705 for EM1-MB and EM4-MB respectively. Whereas, the correlation coefficient (R) for COD removal efficiency versus mudballs' diameter is 0.9549 and 0.9675 for EM1-MB and EM4-MB respectively. These values indicate a significant correlation between TSS as well as COD removals against mudballs' diameter, where increasing mudball diameter results in better removal efficiencies of COD and TSS. This is understandable as COD removal is attributed to both physical (sorption) and biodegradation processes, whereas TSS removal is attributed to physico-sorption processes alone [2]. Hence larger mudball diameters would provide more sorption sites that adsorbed the organic material and suspended solids contained in the artificial river water, resulting in better removal efficiencies.

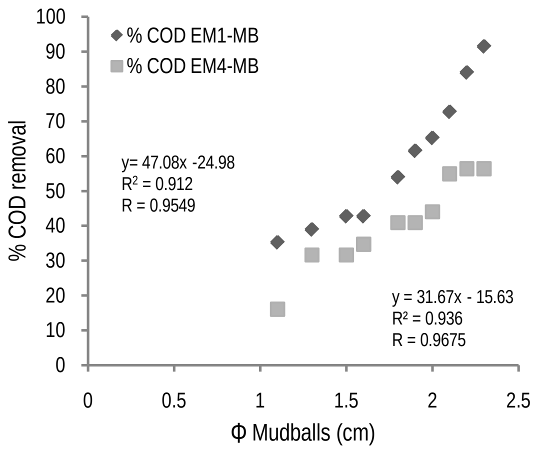

Fig. 3 Correlation between COD removal efficiency and mudballs' diameter

3.2 Adsorption of TSS

Figure 4 depicts the TSS adsorption (mg/g) by different quantities of EM1-MB and EM4-MB after 3 days of incubation at 30°C.

As shown in Fig. 4, TSS adsorptions by both EM1-MB and EM4-MB are higher at lower quantities of mudballs. Given that adsorption of the TSS involves migration by pore diffusion of the TSS from the surface into the interior of the porous adsorbent, it is understandable that more TSS can move into the smaller sized less compacted mudballs in comparison to the larger sized, dense and heavier mudballs [2]. However, as indicated in Fig. 2 removal efficiency is greater with larger sized mudballs, given that the adsorption mechanism for TSS removal by the mudballs entails a surface phenomenon and larger diameters will provide more sorption sites.

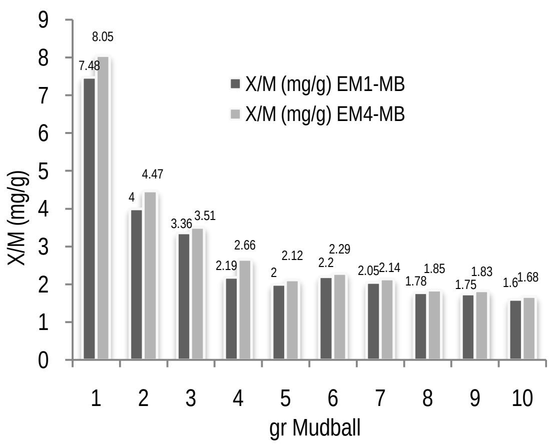

Fig. 4 Adsorption of TSS (mg/g) by different quantities of EM1-MB and EM4-MB at 30°C, C_0 = 100 mg/L

The experimental data were plotted against the Freundlich, Langmuir and BET isotherm models in order to describe TSS adsorption by the mudballs. Table 3 presents the results obtained from this exercise.

Table 3 Calculated isotherm parameters and regression coefficients (R) for TSS adsorption by EM1-MB and EM4-MB

Isotherm	EM1-MB	EM4-MB
Freundlich	n = 1.373	n = 1.212
	K_F = 18.509	K_F = 14.26
	R=0.7714	R =0.8240
Langmuir	Q_m = 0.1041	Q_m = 7.52
	K_L = 67.32	K_L = 0.0168
	R =0.8231	R = 0.8619
		R_L = 0.373
BET	q_m = 32.42	q_m = 2.19
	R = 0.8394	R =0.7211

The regression coefficients (R) presented in Table 3 suggest that TSS adsorption by EM1 mudballs better fits the BET isotherm adsorption model, with q_m=32.42mg/g, Whereas, that with EM4 mudballs better fits the Langmuir isotherm adsorption model, with Q_m= 7.52 mg/g and K_L = 0.0168 L/mg. The BET isotherm is an extension of the Langmuir isotherm that accounts for adsorption by multiple layers of adsorbate, which appears to be the case of EM1 mudballs as the mudballs themselves consisted of a mixture of rice bran and clay soil. The Langmuir isotherm accordingly applies to each layer of adsorbate. In the case of the Langmuir isotherm, its' essential feature is a dimensionless parameter known as the separation factor or equilibrium parameter, R_L, defined as follows [13]:

$$R_L = \frac{1}{1+K_L C_o} \tag{4}$$

where K_L is the Langmuir constant (L/mg) and C_o is the initial concentration of the adsorbate (mg/L). Lower R_L values indicate that the adsorption is favorable, with the shape of the isotherm being either irreversible (R_L=0), favourable (0<R_L<1), linear (R_L=1), or unfavourable (R_L>1) [13]. Hence the R_L = 0.373 indicates that adsorption of TSS by EM4-MB is indeed favorable.

4. CONCLUSION

Batch experiments were conducted at 30°C to study differences in removal efficiencies of 120 mg/L COD and 100 mg/L TSS in artificial river water by 2.5 cm Φ mudballs made from rice bran and clay soil that were inoculated with two different types of activated effective microorganisms (EM) solutions, these being either EM1 which is the original EM solution developed by Dr. Higa in the 1980s or EM4 solution, which is a local EM solution fabricated in Indonesia. Statistical hypothetical testing at α = 0.05 indicates that there is no difference in removal efficiencies of COD and TSS by mudballs made with either EM1 or EM4 activated solutions. However measurements of pH values show that whereas the final pH value of EM4-MB treated artificial river water is in the acidic range (i.e. pH = 4.8), that treated with EM1-MB has a pH value of 6.2 which is within the pH range required by statutory Indonesian regulations for surface water, this being 6-9. The differences in pH values produced by EM1-MB and EM4-MB are attributed to differences in microbial consortia present in EM1 and EM4 solutions. The adsorption mechanism of TSS by EM1-MB is better described by the BET isotherm, which is an extension of the Langmuir isotherm that indicates adsorption by multiple layers of adsorbate, with the Langmuir isotherm applying to each layer of adsorbate. The q_m value of TSS adsorbed by EM1-MB is 32.42 mg/g. With regards to EM4-MB, the results indicate that the adsorption mechanism of TSS by EM4-MB appear to better fit the Langmuir isotherm, which is based on monolayer coverage on a homogenous material. The Langmuir parameters obtained for EM4-MB were Q_m = 7.52 mg/g; K_L = 0.0168 L/mg and R_L = 0.373. This latter R_L value indicates favorable adsorption. The results of this study also show that mudball diameter affects removal efficiencies of COD and TSS where increasing diameters produce better removal efficiencies. The correlation coefficient (R) for COD removal efficiency against mudball diameter was 0.9548 and 0.9675 for EM1-

MB and EM4-MB respectively. The correlation coefficient (R) for TSS removal efficiency against mudball diameter was 0.9633 and 0.9705 for EM1-MB and EM4-MB respectively. Based on the above results, it can be surmised that EM1 activated solution would be the preferred EM solution for the direct treatment of polluted surface water, as pH value of the treated surface water would still meet statutory Indonesian regulations. The mudballs' diameter should also be adjusted to obtain optimum results.

5. ACKNOWLEDGEMENTS

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