# Effect Of Temperature On Removal Of COD and TSS From Artificial River

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# EFFECT OF TEMPERATURE ON REMOVAL OF COD AND TSS FROM ARTIFICIAL RIVER WATER BY MUDBALLS MADE FROM EM4, RICE BRAN AND CLAY

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**ABSTRACT:** In Indonesia surface water is often polluted by domestic waste causing degradation of river water quality. The use of activated Effective Microorganism Solution (EMS) mixed with rice bran or wheat bran, as well as soil and shaped into mudballs has in recent years shown promise as a direct method to improve quality of polluted river water. This study examined the effect of temperature on removal of COD and TSS by mudballs made from activated EM4 solution, rice bran and clay soil. Batch experiments treating artificial river water by the mudballs were conducted at temperatures 25ºC and 30ºC with the artificial river water having initial levels of 120 mg/L COD and 100 mg/L TSS. Efficiency removals of COD by 2.5 cm $\phi$ mudballs at 25ºC and 30°C were 66.7% and 59.4%, whereas that of TSS were 100% and 99.7% respectively. TSS sorption by the mudballs appears to better fit the Langmuir than the Freundlich isotherm models. At 25ºC and 30°C, maximum sorption ($Q_m$) of TSS is 6.89 mg/g and 7.52 mg/g; Langmuir constant ($K_L$) is 0.0196 L/mg and 0.0168 L/mg, while equilibrium parameter ($R_L$) is 0.338 and 0.373 respectively. Statistical hypothesis testing of the experimental data suggests that at $\alpha$=0.05, temperature affects removal efficiency of COD but not that of TSS.

*Keywords: Adsorption Isotherm, 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]. In Indonesia surface water such as rivers is often polluted by both domestic as well as industrial waste, thus causing degradation of river water quality and making it aesthetically displeasing. For example, the average COD and TSS levels of Cikapundung River, Bandung City, West Java, Indonesia in 2013 were 120 mg/L and 100 mg/L respectively; with maximum levels of COD and TSS at times reaching as high as 400 mg/L and 350 mg/L respectively. Although conventional physical-biological treatment methods can be applied to treat polluted river water, they are often costly and not eco friendly [2]. Hence, in recent years the use of Effective Microorganisms (EM) has shown promise as a direct method for improving or restoring polluted river water quality. EM itself is a mixed culture of naturally occurring effective, beneficial, nonpathogenic microorganisms capable of purifying and reviving nature [3]. The concept of EM was first developed by Professor Dr. Teruo Higa of the University of Ryukus, Okinawa Japan [4]. EM has been used in water and sewage purification, improvement of recycled water and solving sanitary problems. As such, EM is also used in the preparation of "Mudballs" or "Bokashi-balls", made from activated EM solution mixed with either rice or wheat bran as well as ordinary dry clay soil and then shaped into balls called "Mudballs" that are left to ferment for about a week. Thereafter, the "Mudballs" are thrown into rivers with the aim of improving river water quality [3]. This technique has been tried out in countries such as Malaysia, Singapore and South Africa. Theoretically, the "Mudballs" act as a sorbent to remove turbidity, while the community of EM heterotrophic microorganisms degrade organic pollutants. Thus, the Mudballs assist in reducing suspended solids, turbidity as well as COD, and improving DO levels of the river water. Rusmaya et al. [5] reported that mudballs made from EM4 mixed with rice bran and clay soil were capable of reducing the TSS and COD concentrations of artificial river water solution. The mixed culture of microorganisms in the EM4 consisted of both Gram negative and Gram positive rod shaped bacteria, some of which were spore-forming, as well as *Mucor sp.* and *Penicillium sp.* fungi and actinomycetes.

The objective of this present study was to examine the effect of different temperatures on the removal of COD and TSS in artificial river water by mudballs made from EM4, rice bran and clay soil, thus determining whether mudballs can be used to improve river water quality under fluctuating temperatures. Given that TSS removal is believed to be achieved by adsorption, the equilibrium data of the TSS removal was also analysed using the Langmuir and Freundlich adsorption isotherm models in order to determine the adsorption capacity for TSS by the mudballs.

## 2. METHODS

All experiments were conducted as batch experiments. COD was measured by closed reflux titrimetry, whereas TSS was measured by gravimetry methods.

### 2.1 Materials

The EM4 used in the experiments was manufactured by Songgo Langit Persada and was bought locally in Bandung, Indonesia. As EM4 is sold in a dormant state, activation of the latter followed the procedure established by Rusmaya et al. [5], this being by diluting 5% EM4 solution with distilled water and left to ferment for a day at room temperature.

The mudballs were prepared by mixing 20% rice bran and 80% dry clay soil with 40% activated EM4 solution (v/w), which was then left to ferment in covered baskets for 7 days at room temperature.

Based on the procedure established by Rusmaya et al. [5], the artificial river water was prepared by adding glucose and 60 mesh sieved kaolin powder into tap water and adjusting the pH of the solution to 4. The initial COD value of the artificial river water was 120 mg/L; whilst initial TSS value was 100 mg/L.

### 2.2 Experiments

*2.2.1 Batch experiments for COD and TSS removal*

The batch experiments on COD and TSS removal were carried out in 250 mL Erlenmeyer flasks under 2 different temperatures, this being 25°C and 30°C. For this, 2.5 cm ϕ mudballs were added into flasks containing 200 ml artificial river water. The experimental flasks were then placed in a shaker water bath which was adjusted to either 25°C or 30°C. The COD and TSS concentrations of the artificial river water were measured daily until no further reduction of COD and TSS occurred.

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 mudballs (1 - 10 g) were then added into the TSS solution and the flasks placed in a shaker water bath adjusted to either 25°C or 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 and Langmuir 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. The mathematical expression of the Freundlich isotherm is as follows:

$$\frac{X}{M} = K_F C_e^{\frac{1}{n}} \quad (1)$$

where $\frac{X}{M}$ is the amount of adsorbate adsorbed by the adsorbent, $K_F$ 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 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:

$$\frac{X}{M} = \frac{Q_m K_L C_e}{1+K_L C_e} \quad (2)$$

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).

## 3. RESULTS AND DISCUSSION

### 3.1 Effect of Temperature on COD and TSS Efficiency Removal

Table 1 shows the effect of temperature on COD and TSS efficiency removal by the mudballs. As shown in Table 1 maximum COD removal was attained within 5 days; whereas all TSS was removed after 3 days.

Table 1 COD and TSS efficiency removal at 25° and 30°C

| Day | % COD removal | | % TSS removal | |
|---|---|---|---|---|
| | 25°C | 30°C | 25°C | 30°C |
| 0 | 0 | 0 | 0 | 0 |
| 1 | 39.2 | 31.2 | 56.7 | 48.7 |
| 2 | 44.2 | 48.9 | 73.3 | 82.7 |
| 3 | 47.5 | 44.8 | 100 | 99.7 |
| 4 | 62.5 | 53.1 | 100 | 99.7 |
| 5 | 67.5 | 59.4 | | |
| 6 | 67.5 | 59.4 | | |

The results also show that although after 5 days the COD levels at both 25°C and 30°C decreased, slightly better COD removal was attained at 25°C. COD efficiency removal at 25°C was 67.5%, whereas COD removal efficiency at 30°C was 59.4%. COD removal is attributed to biosorption followed with degradation of the organic matter by the EM4 microorganisms in the mudballs. As reported in an earlier paper, the EM4 solution consisted of a mixed culture of Gram negative and Gram positive rod shaped bacteria, some of which were spore-forming, as well as *Mucor sp.* and *Penicillium sp.* fungi and actinomycetes [5]. These are heterotrophic, mesophilic microorganisms. Mesophiles grow best at moderate temperatures, typically between 20° and 45°C. Each microorganism have their own optimum temperature for growth and metabolism. In this regard, the consortia of microbes in the EM4 solution appear to grow and carry out metabolism slightly better at 25°C than 30°C. To further confirm this assumption, statistical hypothesis testing of the experimental data was carried out.

Table 2 Statistical hypothesis testing of experimental data

| | % COD removal | % TSS removal |
|---|---|---|
| α | 0.05 | 0.05 |
| Hypothesis | $H_0$: $\mu_{25°C}=\mu_{30°C}$<br>$H_1$: $\mu_{25°C}>\mu_{30°C}$ | $H_0$: $\mu_{25°C}=\mu_{30°C}$<br>$H_1$: $\mu_{25°C}>\mu_{30°C}$ |
| Results of t testing | $t_{calculated}>t_{table}$ | $t_{calculated}<t_{table}$ |
| Conclusion | % COD removal at 25°C > % COD removal at 30°C | % TSS removal at 25°C = % TSS removal at 30°C |

The results are summarised in Table 2, indicating that at α = 0.05, temperature affects removal efficiency of COD, with better COD removal obtained at 25°C.

Figure 1 below shows the comparison in COD removal when only rice bran (RB) mixed with clay soil (CS) were used as sorbent to remove COD, versus mudballs (MB) made from EM4, rice bran and clay soil. As shown in Fig.1 at both temperatures of 25°C and 30°C greater removal of COD was obtained with mudballs in comparison to that obtained with RB + CS. Accordingly, given these results COD removal can therefore be attributed to both physical (sorption) as well as biological process (biodegradation). In fact, the mixed RB+CS can even add to the COD content of the solution (Fig. 1), as RB is organic in nature and can dissolve into the solution. It appears that the presence of fungal mycelia in the mudballs prevent the mudballs from quickly dissipating into the solution, which could increase the COD of the solution.

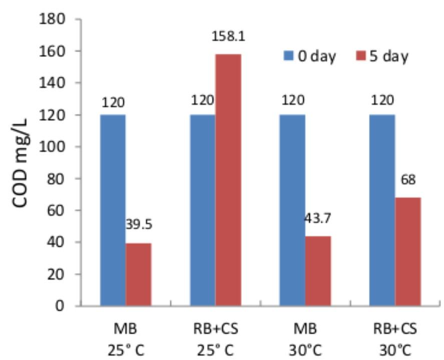


Figure 1 COD removal by MB (Mudballs) versus RB (rice bran) + CS (clay soil) at 25°C and 30°C, $C_0$ of COD=120 mg/L

With regard to TSS removal, 100 % removal by the mudballs was achieved within 3 days (Table 1). Given that in this study the TSS was derived from kaolin, TSS removal is therefore attributed to physico-chemical process, this being by adsorption. Accordingly, TSS removal by 2.5 cm ϕ mudballs was more rapid and efficient than COD removal as the latter is attributed to physico-biological activity which is slower than physico-chemical reactions. Differing from COD, statistical testing of the experimental data indicates that there is no difference in TSS removal efficiency at 25°C and 30°C (Table 2).

### 3.2 Adsorption of TSS

Figures 2 and 3 depict the TSS adsorption ($\frac{X}{M}$ mg/g) and TSS removal efficiency (%) by different quantity of mudballs under different temperatures (i.e 25°C and 30°C).

As shown in Fig. 2, under both temperatures adsorption of TSS is higher at lower amounts of mudballs. Three consecutive mass transport steps are involved in the adsorption of adsorbate from solution by a porous adsorbent. First, the adsorbate migrates through the solution to the exterior surface of the adsorbent particles by film diffusion, followed by solute movement from the particle surface into the interior site by pore diffusion and finally the adsorbate is adsorbed into the active sites at the interior of the adsorbent particle [9]. Hence, smaller quantity of mudball allows tbe adsorbate to move more easily from the surface into the interior as the interior of the adsorbent is less compacted in comparison to the more dense, heavier and thicker mudballs. As such, under such conditions, more adsorbate can be adsorbed with smaller sized mudballs.

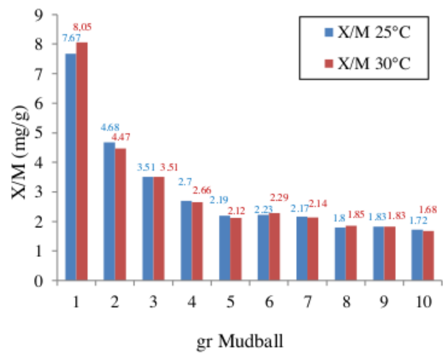


Figure 2 Adsorption of TSS (mg/g) by different quantities of EM4 mudballs at 25°C and 30°C, $C_0$=100 mg/L

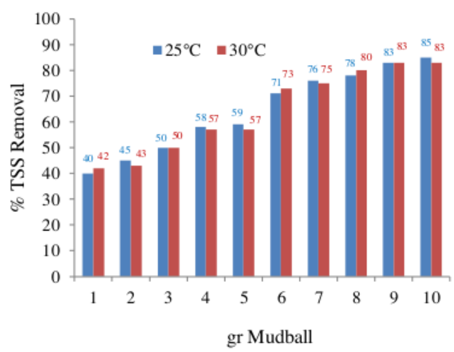


Figure 3 Removal efficiency of TSS by different quantities of EM4 mudball at 25°C and 30°C, $C_0$=100 mg/L

With regard to TSS removal efficiency, Fig. 3 shows that at both temperatures, increasing amounts of mudballs produce better TSS removal efficiency. Increasing the quantity of the mudballs resulted in larger diameter mudballs, which in turn provided more surface areas for adsorption of the TSS. Hence, removal efficiency is greater with larger sized mudballs, given that adsorption is a surface phenomena.

The experimental data were plotted against the Freundlich and Langmuir isotherm models in order to determine which of these two models better describe TSS adsorption by the mudballs. Table 3 presents the results obtained from this exercise.

The regression coefficients ($R^2$) shown in Table 3 suggest that TSS adsorption by the mudballs at temperatures 25°C and 30°C can better be described by the Langmuir isotherm model. As such, at 25°C and 30°C temperatures, maximum adsorption ($Q_m$) of TSS by the mudballs is 6.89 mg/g and 7.52 mg/g respectively; while the Langmuir constant ($K_L$) is 0.0196 L/mg and 0.0168 L/mg respectively.

Table 3 Calculated isotherm parameters and regression coefficients for TSS adsorption by mudballs

| | Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|---|
| | $Q_m$ mg/g | $K_L$ | $R^2$ | n | $K_F$ mg/g | $R^2$ |
| 25°C | 6.89 | 0.0196 | 0.737 | 1.212 | 0.155 | 0.721 |
| 30°C | 7.52 | 0.0168 | 0.743 | 1.212 | 0.153 | 0.679 |

According to Hall, *et al*. [10] the essential features of the Langmuir adsorption isotherm is expressed by a dimensionless constant known as the separation factor or equilibrium parameter $(R_L)$, which is defined as follows:

$$\boldsymbol{R_L} = \frac{1}{1+K_L C_0} \quad (3)$$

The $\boldsymbol{R_L}$ indicates the shape of the isotherm to be either irreversible ($R_L$=*0*), favourable (*0*<$R_L$<*1*), linear ($R_L$=*1*), or unfavourable ($R_L$>*1*). The $R_L$ of this study is given in Table 4.

Table 4 $R_L$ of TSS adsorption by mudballs

| | 25°C | 30°C |
|---|---|---|
| $R_L$ | 0.338 | 0.373 |

The results given in Table 4 show that adsorption of TSS by mudballs at both temperatures are indeed favourable to the Langmuir isotherm. A lower $R_L$ value reflects the adsorption nature to be more favourable [11].

## 4. CONCLUSION

Removal of COD and TSS from artificial river water was achieved in batch experiments by mixing artificial river solution having initial COD of 120 mg/L and TSS of 100 mg/L with mudballs made from activated EM4 solution mixed into rice bran, as well as clay soil and shaking the experimental flasks in a water bath adjusted to 25°C and 30°C. Statistical hypothetical testing shows that the lower temperature produced better COD removal, but that differences in temperature did not affect TSS removal. COD removal by the mudballs is attributed to adsorption followed by biodegradation, whilst TSS removal is by physical process only. Although COD removal was obtained at both 25°C and 30°C, the mesophilic EM4 microorganisms appear to carry out metabolism slightly better at 25°C. Smaller quantity of mudball increased adsorption of TSS, however more TSS removal efficiency was achieved with increasing quantity of mudball, which resulted in larger diameter mudballs. The adsorption mechanism of TSS is better described by the Langmuir isotherm model. At 25°C and 30°C the Langmuir parameters of $Q_m$ are 6.89 mg/g and 7.52 mg/g, and $K_L$ is 0.0196 L/mg and 0.0168 L/mg respectively. $K_L$ represents binding energy, hence the energy of adsorption appears to be slightly larger at 25°C. The equilibrium parameter ($R_L$) obtained at 25°C and 30°C, i.e. 0.338 and 0.373 respectively, indicates that the adsorption is favourable to the Languir isotherm model. The results of this study also suggest that diameter of the mudballs will affect TSS removal efficiency.

## 5. ACKNOWLEDGEMENTS

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