

## **A Quantitative Evaluation of the Effect of Toxic Metals on Biochemical Oxygen Demand**

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**Abstract :** The objective of this study is to employ a quantitative approach to evaluate the relative inhibitory effect of toxic metals, namely Zn, Pb, Cd and Cu, singly and in combination on biochemical oxygen demand (BOD) exertion. Domestic wastewater sample was spiked with the metals singly and in combination in the concentration range of 1 – 50 mg/L for daily BOD determination over a 10-day period. The BOD values with and without metals were fitted to the first-order kinetic model to obtain the rate constants and ultimate BOD values. A toxicity coefficient defined as the fractional reduction in the ultimate BOD values was employed to determine the relative inhibitory effect of the metals and was found to increase in the order: Zn<Pb<Cd<<Cu. The overall inhibitory effect seemed to be determined by the most toxic metal, namely Cu, and no synergistic effect of metals was observed. An empirical relationship between the toxicity coefficient and metal concentration was proposed.

**Abstrak :** Objektif kajian ini adalah untuk menggunakan suatu pendekatan kuantitatif untuk menilai kesan pencegahan relatif bagi metal toksik, iaitu Zn, Pb, Cd dan Cu, secara individu dan bercampur terhadap tuntutan oksigen biokimia (BOD). Sampel air buangan domestik telah ditambahkan logam individu dan juga bercampur dalam julat kepekatan 1 – 50 mg/L untuk penentuan BOD harian selama tempoh 10 hari. Nilai BOD dengan dan tanpa logam telah disesuaikan dengan model kinetik tertib pertama untuk memperoleh nilai pemalar kadar dan BOD terakhir. Satu pekali ketoksikan yang ditakrifkan sebagai pengurangan pecahan dalam nilai BOD terakhir digunakan untuk menentukan kesan pencegahan relatif logam dan didapati nilai pekali itu meningkat mengikut turutan: Zn<Pb<Cd<<Cu. Kesan pencegahan keseluruhan nampaknya ditentukan oleh logam yang terlalu toksik, iaitu Cu, dan kesan sinergistik bagi logam tidak diperhatikan. Suatu perhubungan di antara pekali ketoksikan dengan kepekatan logam dicadangkan.

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### **Introduction**

Biochemical oxygen demand (BOD) is recognized as one of the most important parameters in assessing organic pollution in aquatic systems. The standard BOD testing procedure involves incubating a sample, diluted or otherwise, over a 5-day period at 20 °C and determining the amount of dissolved oxygen used by microorganisms for the biochemical oxidation of carbonaceous organic matter. The result of BOD test is therefore very much dependent on the types of constituents present in the tested sample which may influence the bioactivity of microorganisms. Thus, the BOD value is affected by environmental factors such as temperature, salinity, pH and may be repressed by the presence of chlorine, metals and organic compounds which inhibit the bioactivity of microorganisms.

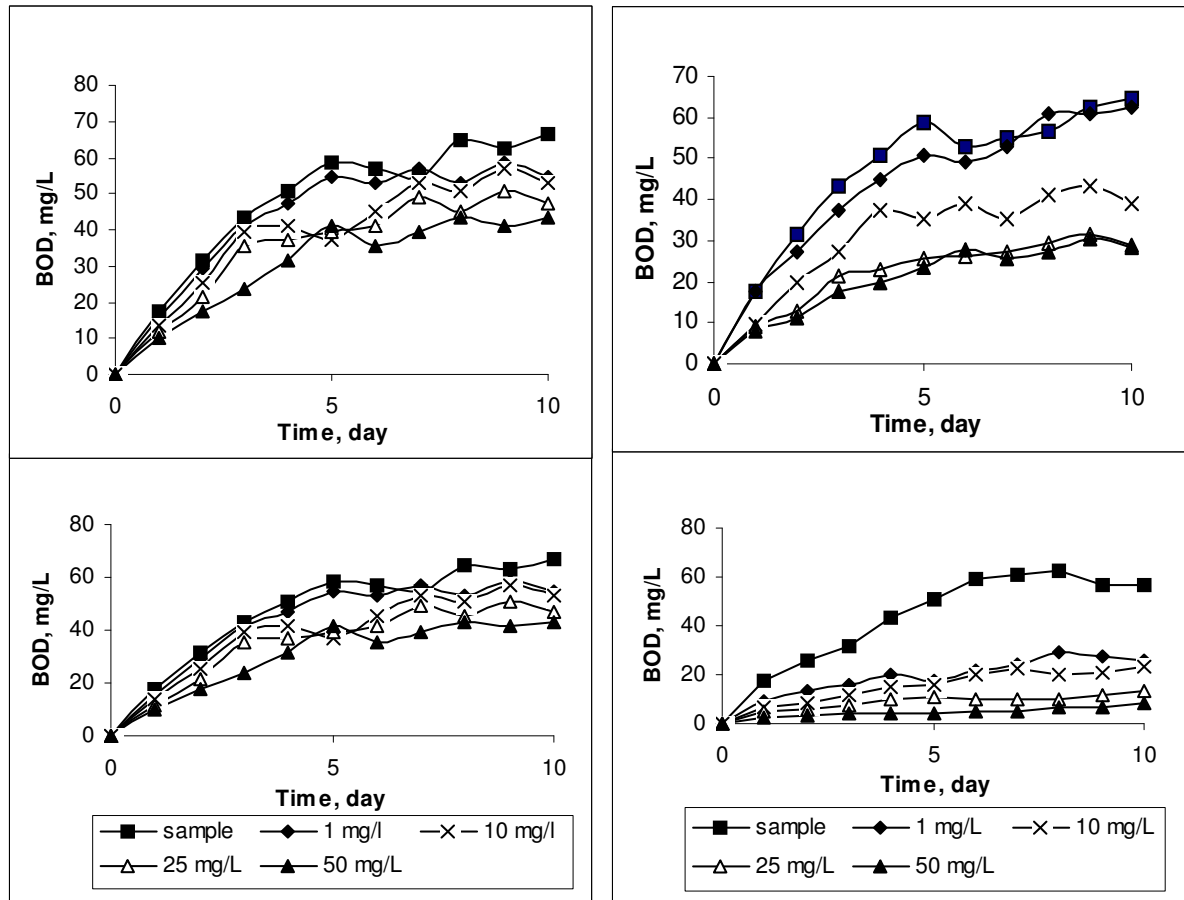
Over the years, much research work had been conducted to investigate the effect of temperature [1-3], salinity [4], chlorination [5] and metals [6-9] on BOD exertion. In particular, previous reported work on the repression of BOD due to the toxicity of metals singularly or in combination has always been qualitative in approach. The objective of this study is to employ a quantitative approach in evaluating the relative inhibitory effect of toxic metals like Zn, Pb, Cd and Cu singly and in combination on BOD

exertion. This kind of approach is far less ambiguous and the information derived might be useful in the field of water pollution caused by metals.

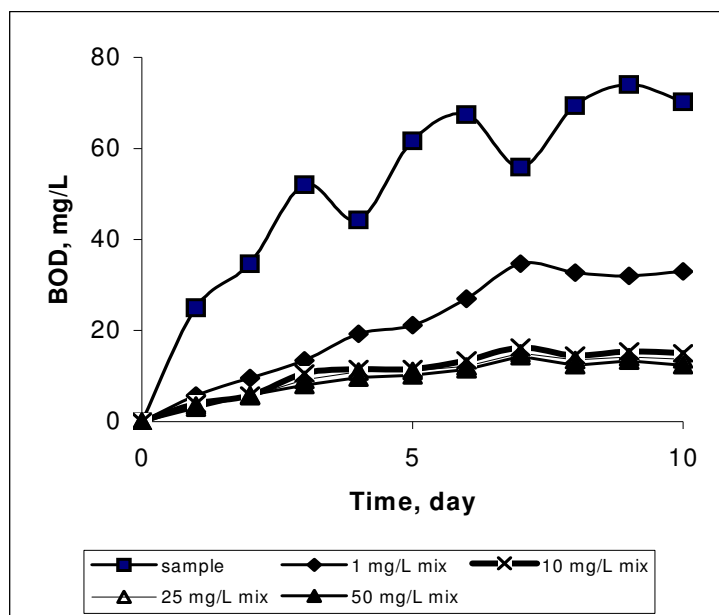
### **Materials and Methods**

Domestic wastewater samples were collected from the sewage treatment plant located in the Universiti Sains Malaysia campus. Based on the results of the COD test [10], appropriate dilution of the wastewater sample was made using dilution water saturated with dissolved oxygen (DO). In addition to the nutrients, 5 mL of 5 mg/L N-allylthiourea solution was added to each litre of diluted test sample to inhibit nitrification. The sample was placed in sufficient number of BOD bottles for daily BOD determination over a period of 10 days and the bottles were incubated at 20 ± 0.1 °C.

The toxic metals chosen for this study were Zn, Pb, Cd and Cu. For the same diluted wastewater sample, a known quantity of metal ion solution was added in four sets of BOD bottles so that the concentration was 1, 10, 25 and 50 mg/L, respectively. Similarly, for the study on the combined effect of the four metals, four sets of BOD bottles were prepared so that each set contained 1, 10, 25, and 50 mg/L, respectively of each metal. The procedure for initial and daily DO determinations



**Figure 1 :** BOD curves for domestic wastewater before and after the addition of 1, 10, 25 and 50mg/L of (a) Zn, (b) Pb, (c) Cd and (d) Cu.



of Zn, Pb, Cd and Cu at the respective concentrations of 1, 10, 20 and 50 mg/L. followed the Winkler's method described in the Standard Methods [10].

### Results and Discussion

Figures 1(a) – (d) depicts the individual effect of Zn, Pb, Cd and Cu on BOD exertion in increasing metal concentrations, respectively, whereas Fig. 2 shows the combined effect of the four metals on BOD exertion. The BOD exertion curve is commonly described by the first-order formulation,

$$y = L(1 - e^{-kt}) \quad (1)$$

where  $y$  = BOD at time  $t$   
 $L$  = ultimate BOD  
 $k$  = first-order rate constant.

Despite the fact that the first-order model for BOD exertion does not have any theoretical basis, it is still the most widely employed kinetic model due

to its simplicity. Which kinetic model fits the BOD data best has always been a topic of great interest to the researchers [11-14].

For convenience, the first-order kinetic model was chosen for this study. The BOD values obtained with and without metals were fitted to the first-order model to calculate the  $k$  and  $L$  parameters [15], the values of which are shown in Table 1. The data in Table 1 indicate that the ultimate BOD,  $L$ , rather than the rate constant,  $k$ , provided a more consistent response to increasing metal concentrations. A toxicity coefficient  $E$  is therefore proposed as follows:

$$E = (L_o - L)/L_o \quad (2)$$

where  $L_o$  is the ultimate BOD in the absence of metal. This formulation allows the toxic effect to be normalized. Figure 3 shows the values of  $E$  for Zn, Pb, Cd and Cu singly and in combination as a function of metal concentrations.

**Table 1 :** The values of first-order kinetic parameters at increasing concentrations of Zn, Pb, Cd and Cu singly and in combination.

Metal	Concentration(C), mg/L	Rate constant (k), day <sup>-1</sup>	Ultimate BOD (L), mg/L
Zn	0	0.289	72
	1	0.315	64
	10	0.269	61
	25	0.263	56
	50	0.224	51
Pb	0	0.302	82
	1	0.296	74
	10	0.297	66
	25	0.376	55
	50	0.334	51
Cd	0	0.308	98
	1	0.288	82
	10	0.276	79
	25	0.287	44
	50	0.248	42
Cu	0	0.257	69
	1	0.336	29
	10	0.228	25
	25	0.352	13
	50	0.290	7
Zn, Pb, Cd and Cu	0	0.369	74
	1 for each metal	0.0996	57
	10 for each metal	0.241	20
	25 for each metal	0.242	17

For each metal, a graph of  $E$  versus metal concentration  $C$  can be approximated by the following equation:

$$E = PC/(1 + QC) \quad (3)$$

where  $P$  and  $Q$  are constants. Equation (3) can be linearized to yield:

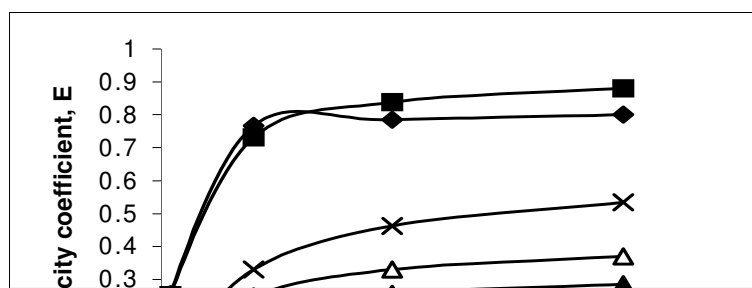
$$C/E = 1/P + QC/P \quad (4)$$

Table 2 presents a summary of the regression analyses including the regression models based on Equation (4) to predict the magnitude of the toxicity coefficient given the concentration of each metal.

Within the concentration range of 1-50 mg/L, the relative inhibitory effect of the metals was found to increase in the order: Zn<Pb<Cd<<Cu and that the synergistic effect of metals was not observed. The observed trend was in agreement

with the results of Mittal and Ratra [8] for Cu, Pb and Zn in the concentration range of 1-10 mg/L, the results of which were based on the inhibition of BOD<sub>5</sub> exertion. The values of toxicity coefficient seemed to approach a plateau, most obviously for Cu, at higher metal concentrations. The explanation can be found in Mittal and Ratra [8] who suggested that the formation of metal oxide along with the normal process of BOD exertion may lead to an anomalously higher DO consumption, thus higher BOD value. This will depress the toxicity coefficient value at high metal concentration. In the case of a combination of metals, the results of this study indicate that the overall inhibitory effect was determined by the most toxic metal, namely Cu.

Further research work needs to be conducted to ascertain whether this quantitative approach is applicable to describe the toxic effect exerted by those metals at lower concentration ranges and in different types of wastewater.



**Figure 3 :** Toxicity coefficient  $E$  versus metal concentration  $C$  for Zn, Pb, Cd and Cu.

**Table 2 :** Regression analyses for toxicity coefficient  $E$  versus metal concentration  $C$  for Zn, Pb, Cd and Cu

Metal	Regression model	Coefficient of determination, $R^2$
Zn	$C/E = 19.70 + 3.115C$	0.967
Pb	$C/E = 16.48 + 2.372C$	0.977
Cd	$C/E = 14.47 + 1.584C$	0.988

### Conclusions

Based on a toxicity coefficient defined as the fractional reduction in the ultimate BOD value, the relative inhibitory effect of the metals on BOD exertion was found to increase in the order of  $Zn < Pb < Cd < Cu$  in the metal concentration range of 1 – 50 mg/L. In the case of a combination of the four metals, no synergistic effect of metals was observed and the overall inhibitory effect was found to be determined by the most toxic metal, namely Cu.

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