# INVESTIGATION OF ZINC REMOVAL CAPACITIES OF DIFFERENT SORBENT MATERIALS TO BE USED IN CONSTRUCTED WETLANDS

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***ABSTRACT***

It has been found over the past couple of years that health hazards associated with heavy metals have been on the rise, particularly the chronic diseases. Lack of tertiary treatment of wastewater may have contributed to this emergent problem, mainly due to the high costs involved in the removal of heavy metals. Constructed wetlands have therefore received great attention as a tertiary treatment method or a polishing technique of wastewater due to its low construction and operation costs. However, finding a low-cost sorbent material to be used as the wetland filter material, which can be used as an alternative to activated carbon, has been a problem for decades. Therefore, the present study focuses on applicability of low-cost sorbent materials: viz., clay tile, brick, saw dust and rice husks, as filter mediums. Laboratory-scale experiments were performed with a synthetic Zinc solution. Results revealed that clay tile material has the highest adsorption capacity (47.6 mg/g) and removal efficiency, (98%), while brick (37.0 mg/g, 86%), sawdust (20.4 mg/g, 80%) and rice husks (15.8 mg/g, 64%) have relatively low adsorption capacities and removal efficiencies, respectively. The separation factor of equilibrium ($R_L$) indicates favourable isotherms ($0< R_L<1$) for all tested sorbent materials. Among the studied materials clay tile, brick and rice husks are good adsorbents for Zinc (n>2) while sawdust is a moderately difficult material for adsorption of Zinc (n <2).

**Keywords:** adsorption isotherms, constructed wetlands, sorbent material, Zinc

## 1. INTRODUCTION

Contamination of the environment from a variety of heavy metal sources has become an increasingly serious problem in recent years. Industrial and municipal wastewaters frequently contain heavy metal ions (Demirbas et al., 2008) such as lead, copper, cadmium, zinc, and nickel, which are amongst the most common pollutants found in industrial effluents (Djeribi and Hamdaoui, 2008). Heavy metal ions are reported as priority pollutants due to their mobility in natural water ecosystems and toxicity. The heavy metal ions are stable and persistent environmental contaminants since they are neither be degraded nor destroyed (Bozic et al., 2009). Even at low concentrations, these metals can be toxic to organisms, including humans. It is well-known that selective removal of metal ions in dilute solutions is very difficult by conventional wastewater treatment methods. Therefore, it is vital to safeguard public health, the social security and accomplish environmental integrity through the application of reliable but low-cost technologies particularly in developing countries.

Lack of tertiary treatment may have contributed to this growing problem and consequent environmental pollution. Constructed wetlands have therefore received greater attention as a tertiary treatment method or a polishing technique of wastewater due to its low construction and operation costs, minimal maintenance and also because of it is perceived to be an environmental friendly system. Nevertheless, activated carbon has been extensively used for decades, as a good candidate for adsorbing pollutants because porous carbons have a large specific area and a high adsorption capacity, compared with other sorbent materials (Kurniawan et al., 2006). However, varieties of activated carbon are expensive and cannot be regenerated easily. Lately, there has been a growing demand for an efficient and cost-effective sorbent material to be used as an alternative for activated carbon.

In this context, the present work examines the Zinc removal capacities of low-cost sorbent materials that can be used in constructed wetlands as a medium in which vegetation may be grown. To accomplish this, two objectives were defined as:

1. Investigation of maximum sorption capacities of clay tile, brick, sawdust and rice husks by using Langmuir and Freundlich isotherms and
2. Determination of applicable sorbent material(s) to be effectively used in constructed wetlands.

## 2. MATERIALS AND METHODS

### *2.1 ADSORBENT*

The four adsorbents used in this study were: clay tile, brick, sawdust and rice husks. Each sorbent material was obtained from local industries. They were used directly for adsorption experiments without any pre-treatment. Samples were washed thoroughly with distilled water, dried and ground to obtain a fine powder. Then the powder was washed several times with distilled water till clear water was obtained. Thereafter, it was dried in an oven at 105ºC for 24 hrs. The dried powder was then sieved to separate particles less than 415µm in order to obtain a uniform particle size. The materials were placed in vacuum desiccators for further use.

### *2.2 ADSORBATE*

Synthetic Zn solution was used for both the preliminary study and batch experiment. The stock solution of 500 mg/L Zn was prepared using Zinc Sulphate ($ZnSO_4.7H_2O$, analytical grade). Test solutions were prepared from stock solutions with desired dilution with de-ionized water.

### *2.3 BATCH EXPERIMENTS AND ISOTHERM STUDIES*

Batch experiments were carried out in 1L beakers with 250 ml test solution agitated on a horizontal shaker for 24 hrs at 100 rpm at room temperature (28 ± 3 ºC). For each run, 1.0 g of each adsorbent (clay tile, brick, and sawdust and rice husks) was used. The samples were taken at predetermined intervals. At the end of the desired contact time, a beaker was removed from the shaker and allowed for settling the adsorbent. Then, samples were centrifuged and the supernatant was analyzed for residual metal Zn concentration using AAS method, as described in the Standard Methods of Examination of Water and Wastewater (APHA, 1999). Blank runs, with only the adsorbent in 250 ml of deionized water were conducted simultaneously under similar conditions. The amount of metal adsorbed into each adsorbent was calculated by a mass balance equation:

$$Q_e = (C_o - C_e)V/W \quad (1)$$

where $C_o$ and $C_e$ are the initial and equilibrium liquid phase concentrations of the Zn metal (mg/L) respectively, $V$ the volume of the test solution (L) and $W$ the weight of the dry adsorbent (g).

The data for the sorption of Zinc were modelled using Langmuir and Freundlich isotherms.

Adsorption isotherms were determined under equilibrium conditions. The amount of the metal adsorbed into four different adsorbents increased with time (Fig. 1) and reached saturation where no more removal was observed from the solution. At this point, the amount of Zinc being adsorbed onto adsorbent is in a state of dynamic equilibrium with the amount of Zinc desorbing from the adsorbent. The time required to attain half saturation for clay tile, brick, sawdust and rice husks were 75 min, 21min, 49.2 min and 66.6 min respectively. However, adsorption capacities and the removal efficiencies were different: tile material has the highest adsorption capacity (47.6 mg/g) and removal efficiency, (98%) while brick (37.0 mg/g, 86%), sawdust (20.4 mg/g, 80%) and rice husks (15.8 mg/g, 64%) have relatively low adsorption capacities and removal efficiencies, respectively.

## 3 RESULTS AND DISCUSSION

### *3.1 EQUILIBRIUM STUDIES*

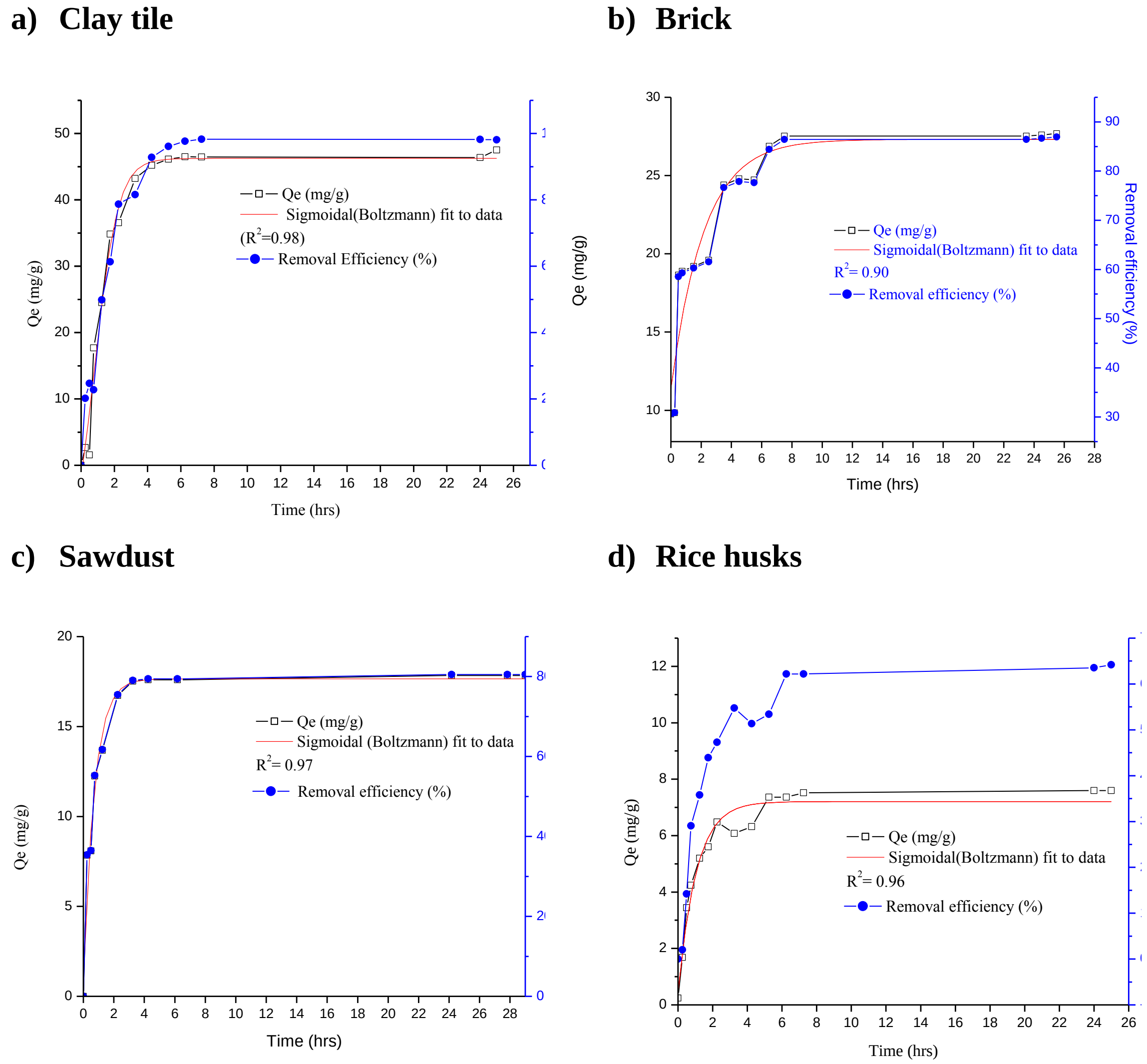


**Figure 1**: The effect of contact time on removal efficiency of adsorbent; a) clay tile, b) brick, c) sawdust, d) rice husks. (Initial concentration - 100 mg/l of Zn, particle size - 415 um, dose - 1 g/100 ml, pH - 6.5)

### *3.2 ISOTHERM STUDIES*

The adsorption equilibrium was described by isotherm equations which often provide some insight into sorption mechanism, surface properties and affinity to sorbent. The Langmuir and Freundlich equations are commonly used in describing adsorption isotherms at a constant temperature for water and waste water treatment applications. Therefore, following two widely used isotherms were applied:

a) b)

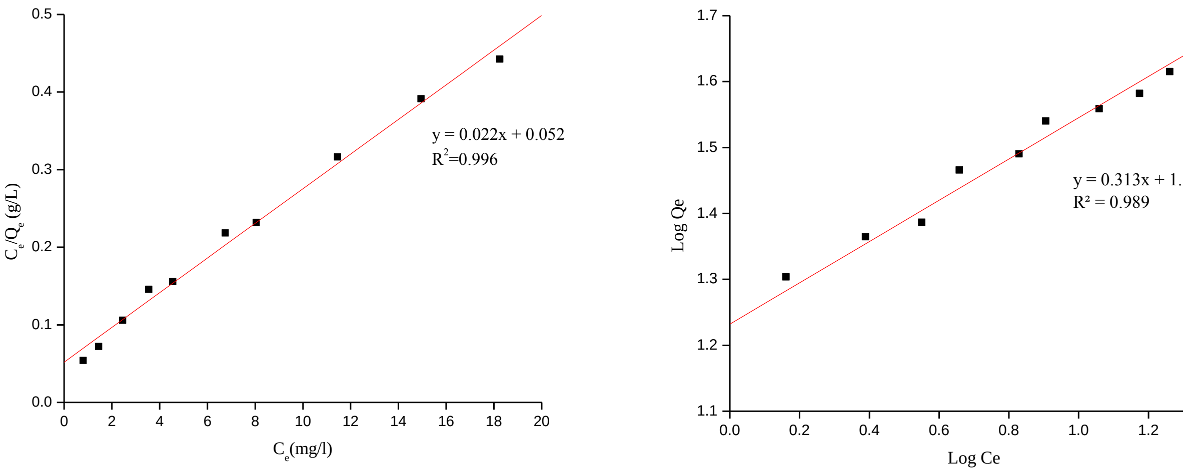


**Figure 2**: Langmuir (a) and Freundlich (b) Isotherms for clay tile at room temperature (28±3ºC).

(a) (b)

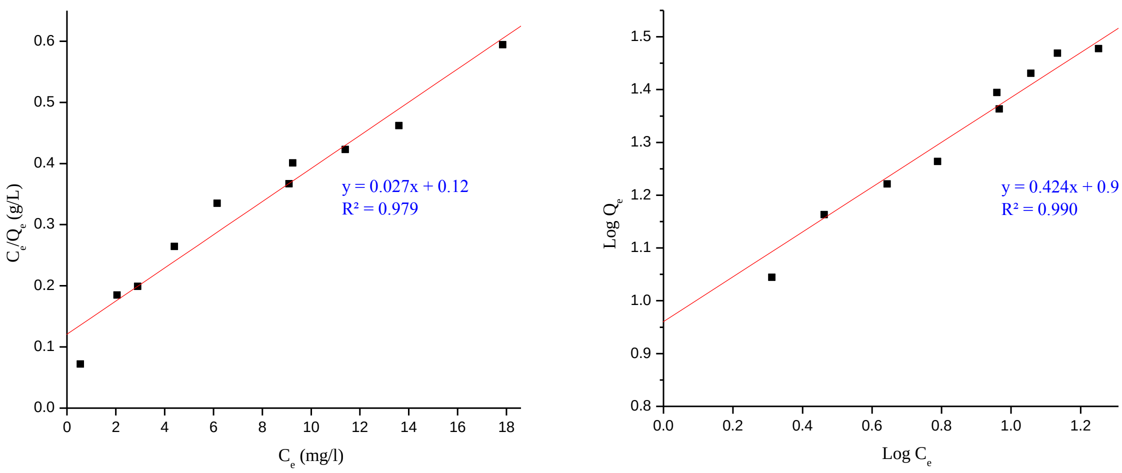


**Figure 3**: (a) Langmuir, and (b) Freundlich Isotherms for brick at room temperature (28 ± 3 ºC).

Langmuir adsorption isotherms: A basic assumption of this theory is homogeneous sites within the adsorbent and monolayer adsorption. The Langmuir model is given by the following equation:

$q_e = QbC_e/1+bC_e$ (2)

and its linearized expression is:

$C_e/q_e = 1/(bq_m)+(1/q_m)C_e$ (3)

where $q_e$ amount of Zinc adsorbed per unit weight of adsorbate (mg/g), $C_e$ is the equilibrium concentration of the solution (mg/L). The $b$ and $q_m$ are Langmuir coefficients representing the equilibrium constant for the adsorbate-adsorbent equilibrium and monolayer capacity of the solid. The values of maximum adsorption capacity determined using linear transformation of the Langmuir equation are higher than the experimental adsorbed amount at the equilibrium and correspond to the adsorption isotherm plateau (Table 1).

The Langmuir equation is also used to obtain $R_L$, the separation factor of equilibrium:

$R_L = 1/ (1+bC_0)$ (4)

Where $C_0$ is the initial concentration of the adsorbate.

(a) (b)

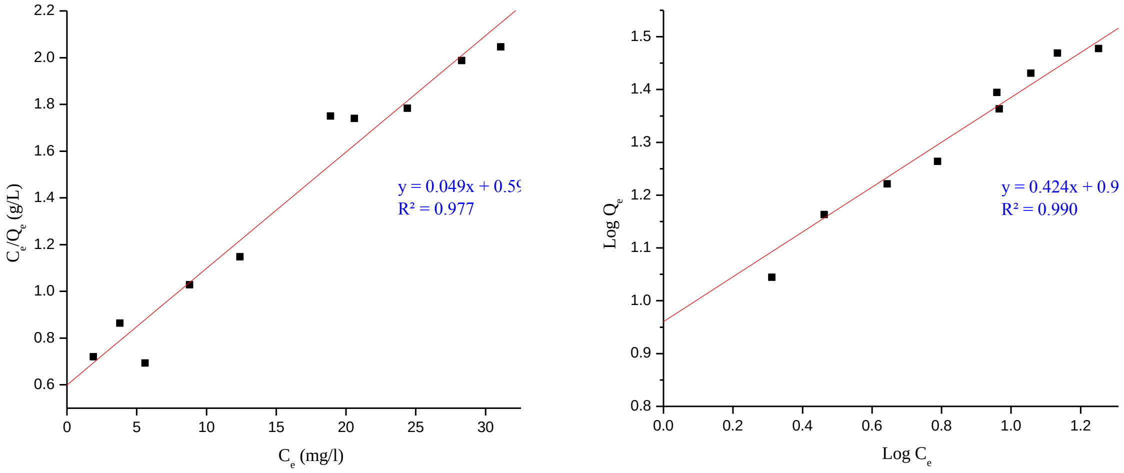


**Figure 4**: (a) Langmuir, (b) Freundlich Isotherms for sawdust at room temperature (28 ± 3 ºC).

(a) (b)

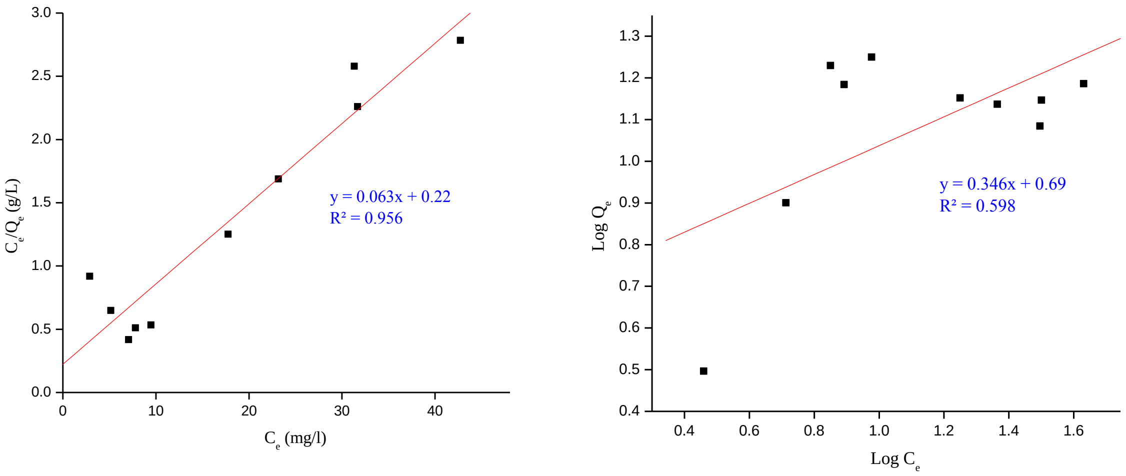


**Figure 5**: (a) Langmuir, (b) Freundlich Isotherms for rice husk at room temperature (28 ± 3 ºC).

The values of RL indicate the type of isotherm to be irreversible ($R_L = 0$), favourable ($0< R_L<1$), linear ($R_L = 1$) or unfavourable ($R_L> 1$).

Freundlich equation based on heterogeneous surface:

Freundlich isotherm: $q_e = KFCe1^{/n}$ (5)

where $K_F$ is the Freundlich constant and $n$ is the Freundlich exponent. A linear form of Freundlich equation is given by:

$\text{Log } q_e = \text{Log } K_F + 1/n \log C_e$ (6)

Based on the correlation coefficient ($R^2$) shown in Table 1, the equilibrium data were correlated with both Langmuir and Freundlich isotherms. However, adsorption isotherms are well-described by Langmuir isotherms. The separation factor of equilibrium ($R_L$) indicates favourable isotherms

(0< $R_L$ <1) for all tested sorbent materials. This further describes that monolayer adsorption of Zinc.

**Table 1:** Langmuir and Freundlich isotherm constant for clay tile, brick, sawdust and rice husks in Zinc solution

| Material | Langmuir constant | | | $R_L$ | Freundlich constant | | |
|---|---|---|---|---|---|---|---|
| | $Q_{max(mg/g)}$ | b (1/mg) | $R^2$ | | $K_F$ | $n$ | $R^2$ |
| Clay tile | 47.6 | 0.403 | 0.996 | 0.113 | 16.98 | 3.19 | 0.989 |
| Brick | 37.0 | 0.225 | 0.979 | 0.305 | 9.12 | 2.35 | 0.990 |
| Sawdust | 20.4 | 0.081 | 0.977 | 0.701 | 2.18 | 1.74 | 0.966 |
| Rice husks | 15.8 | 0.022 | 0.986 | 0.342 | 4.26 | 2.89 | 0.598 |

However, using the Freundlich model similar results can be reported for the sorption of Zinc. The magnitude of the exponent *n* gives an indication of favourability of adsorption. It is stated that *n* in the range between 2-10 represent good, 1-2 moderately difficult and less than 1 poor adsorption characteristics. Among the studied materials, clay tile, brick and rice husks are good adsorbents for Zinc ($n$>2) while sawdust is a moderately difficult material for adsorption of Zinc ($n$ <2).

Selection and identification of an appropriate low cost adsorbent may rely on maximum adsorption of pollutant to the adsorbent. From the present study (Table 2), these low cost materials have shown outstanding adsorption capacities. It is evident that the cost effectiveness of an adsorbent is one of the important factors that needs to be compared with commercially available activated carbon.

**Table 2:** Zn removal capacities of different low-cost sorbent materials and commercial activated carbon

| Adsorbent | Adsorption capacity(mg/g) | References |
|---|---|---|
| Mango peel | 28.2 | Iqbal et al., 2009 |
| Sugar cane baggase | 31.1 | Mohan et al., 2002 |
| Blast furnace slag | 103.3 | Dimitrova (1996) |
| Green sand | 32.4 | Lee et al., (2004) |
| Natural zeolite | 13.0 | Peric et al., (2004) |
| HCL treated clay | 63.2 | Vengris et al., (2001) |
| Clay tile | 47.6 | Present study |
| Brick | 37.0 | Present study |
| Sawdust | 20.4 | Present study |
| Rice husks | 15.8 | Present study |
| Type of commercially available activated carbon | | |
| GAC type carbon | 20.0 | Leyva-Romes et al., (2002) |
| GAC type | 0.29 | Bansode et al., (2003) |

## 4 CONCLUSION

Results revealed that clay tile material has the highest adsorption capacity (47.6 mg/g) and removal efficiency (98%), while brick (37.0 mg/g, 86%), sawdust (20.4 mg/g, 80%) and rice husks (15.8 mg/g, 64%) have relatively low adsorption capacities and removal efficiencies respectively. The separation factor of equilibrium ($R_L$) indicates favourable isotherms (0< $R_L$<1) for all tested sorbent materials. Among the studied materials clay tile, brick and rice husks are good adsorbents for Zinc (n>2) while sawdust is a moderately difficult material for adsorption of Zinc (n <2).

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