ZINC ADSORPTION BY LOWCOST SORBENT MATERIALS: CLAY TILE, BRICK, SAWDUST AND RICE HUSK

Ayoma Witharana*, Mahesh Jayaweera and Jagath Manatunge
Division of Environmental Engineering, Department of Civil Engineering,
University of Moratuwa, Katubedda.
* Corresponding author: E-mail: ayomiwitharana@yahoo.co.uk Tel-++ 94 112 650 567

Abstract: It has been found over the past couple of years rapid growth of population, industrialization and urbanization has first and foremost contributed to the severe water pollution in both surface and ground water. The 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, adsorption process is considered as the best available water treatment method and activated carbon has proven to be the best sorbent material which can be used in removing wide variety of pollutants. However, usage of this activated carbon becomes restrict due to its high cost and regeneration cost. Therefore, the present study focuses on low-cost sorbent materials: viz., clay tile, brick, sawdust and rice husks. 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 adsorbent for Zinc (n>2) while sawdust is a moderately difficult material for adsorption of Zinc (n <2).

Keywords: adsorption capacity, low cost sorbent materials, Zinc

1 Introduction

Rapid growth of population, industrialization and urbanization has first and foremost contributed to the severe water pollution in both surface and ground water. The main sources of freshwater pollution can be attributed to discharge of untreated sanitary and toxic industrial wastes, dumping of industrial effluents, and runoff from agricultural fields (Bhatnagar and Sillanpa, 2010). Heavy metal contamination 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 due to their toxicity. The heavy metal ions are stable and persistent environmental contaminants since they neither be degraded nor destroyed (Bozic et al., 2009). However, selective removal of metal ions in dilute solutions is very difficult by conventional wastewater treatment methods. Therefore, in order to safeguard public health, the social security and accomplish environmental integrity through the application of reliable but low-cost technologies particularly in developing countries.

However, 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). On the other hand, varieties of activated carbon they are expensive and cannot regenerate easily. Later on, there has been a growing demand for an efficient and cost-effective sorbent material to be used as an alternative for activated carbon.

Therefore, the present work investigates the Zinc adsorption capacity for low-cost sorbent materials. To accomplish this, two objectives were defined as:

1. Investigation adsorption behaviours of clay tile, brick, sawdust and rice husks by using Langmuir and Freundlich isotherms and
2. Compare the adsorption behaviour with activated carbon, the industry standard, for Zinc adsorption.

2 Materials and Methodology

The main objective is to develop a cost effective rainwater harvesting system that can be integrated with the central water supply to supplement part of the water used for domestic needs. The following methodology was used:

2.1 Adsorbent

The four low cost 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, 1.000 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 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:

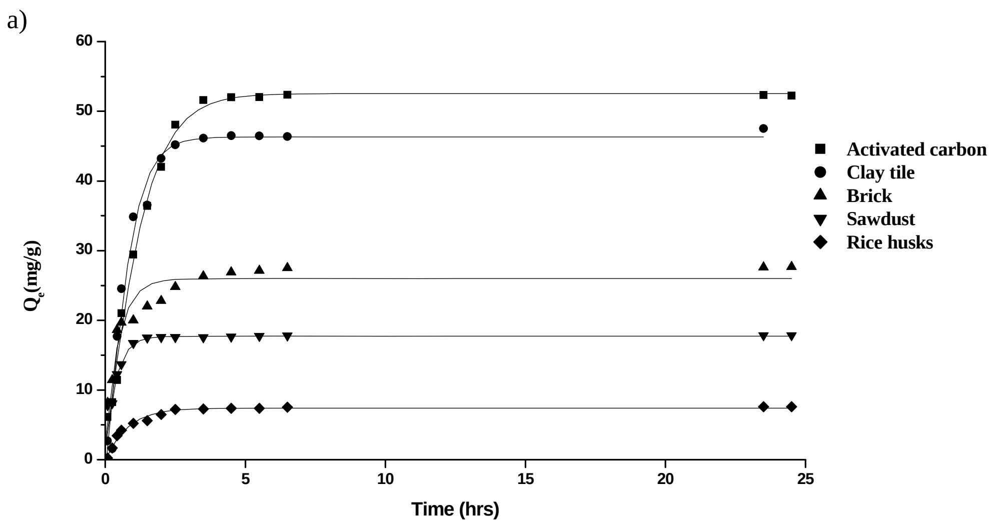
$$Q_e = (C_o - C_e)V/W \qquad (1)$$

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.

3 Results and discussion

3.1 Equilibrium studies and removal efficiency

Adsorption isotherms are in general 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.



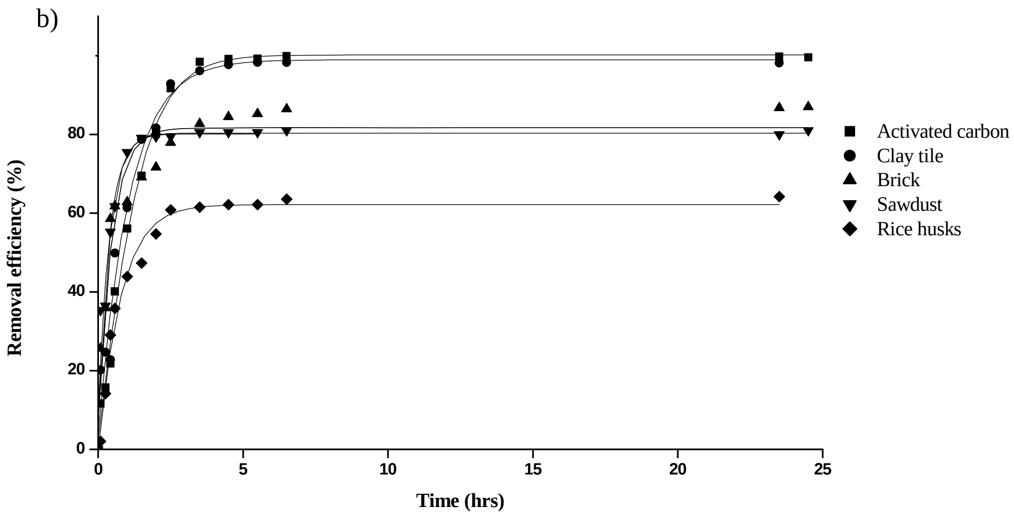


Figure 1: *The effect of contact time on amount adsorbed a) and removal efficiency b) (Initial concentration - 100 mg/l of Zn, particle size - 415 um, dose - 1 g/100 ml, pH - 6.5)*

3.2 Isotherm Studies

The adsorption equilibrium was described by isotherm equations which often provide some insights 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: 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:

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

and its linearized expression is:

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

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:

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

where C_0 is the initial concentration of the adsorbate.

The values of R_L indicates 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: $q_e = K_FC_e^{1/n}$ (5)

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

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

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.

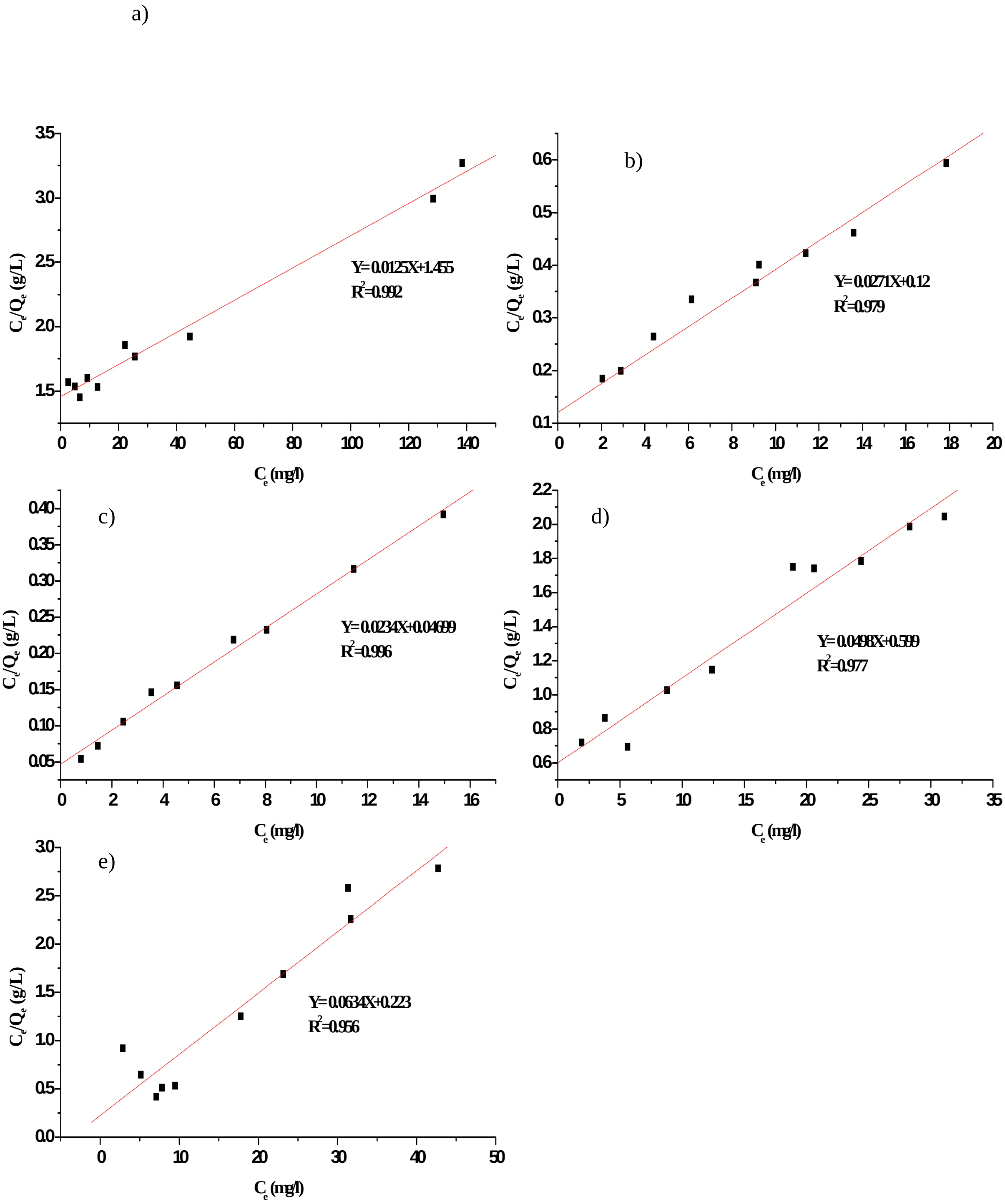


Figure 2: *a) Langmuir Isotherms for a)clay tile, b)brick , c)sawdust d)rice husks and e) activated carbon at room temperature (28 ± 3 ºC).*

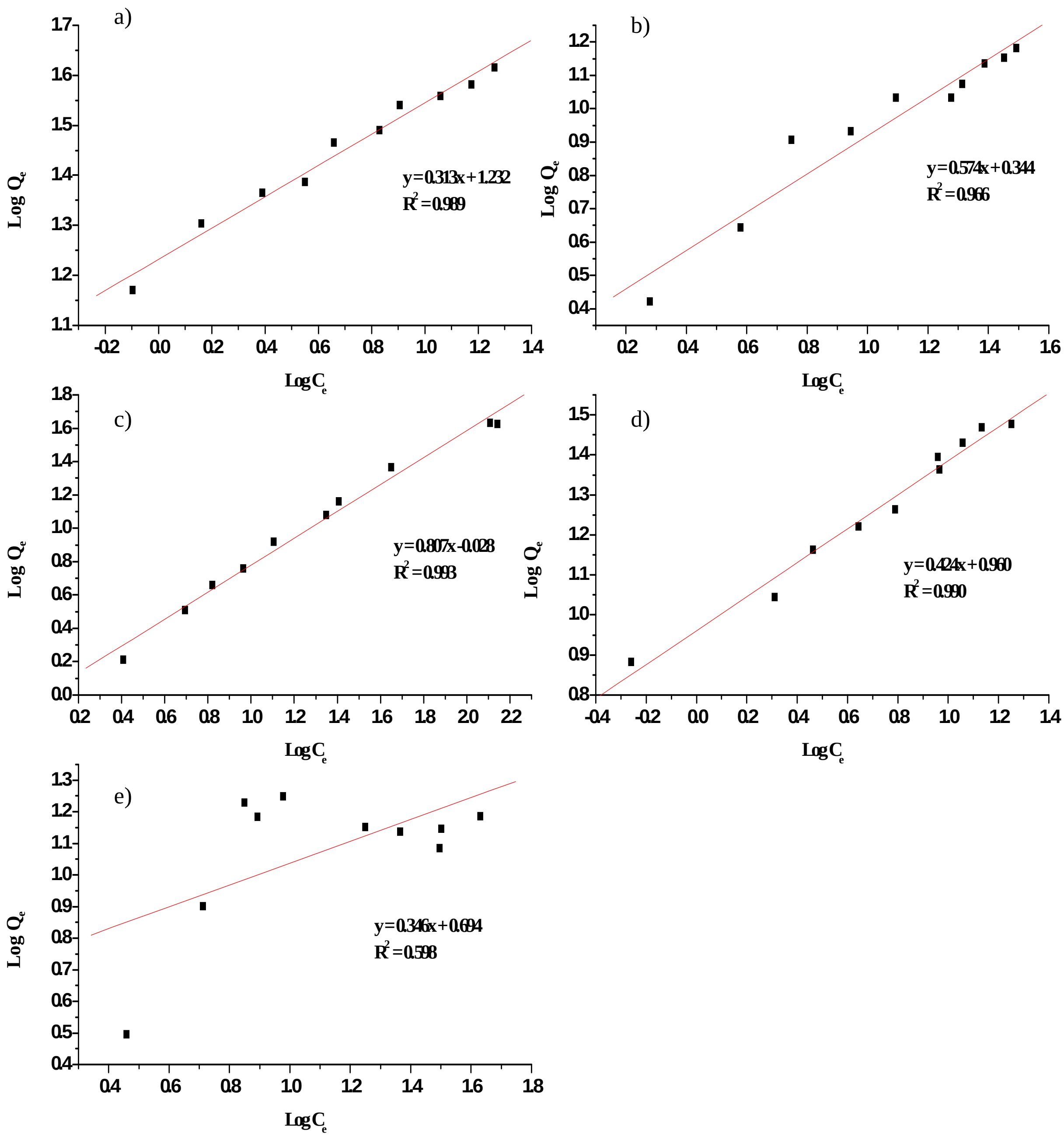


Figure 4: *a) Freundlich Isotherms for a) clay tile, b)brick, c) sawdust d)rice husks and e)activated carbon at room temperature (28 ± 3 ºC).*

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
Activated carbon	80. 0	0.008	0.992	0.952	22.14	4.24	0.993

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 adsorbent for Zinc (n>2) while sawdust is a moderately difficult material for adsorption of Zinc (n <2).
Selection and identification of 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 capacity. 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 adsorbent for Zinc (n>2) while sawdust is a moderately difficult material for adsorption of Zinc (n <2).

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