

ADSORPTION OF Zn(II) FROM AQUEOUS METAL SOLUTIONS BY USING CHEMICALLY MODIFIED AND UNMODIFIED SUGARCANE BAGASSE AS AGRICULTURAL ADSORBENT

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ABSTRACT

Adsorption of heavy metals contaminants from waste water is one of the most important environmental and economic issue today. This paper presented the kinetics of Zn (II) ions adsorption from aqueous solutions, using chemically modified sugarcane bagasse (MSB) and unmodified sugarcane bagasse (USB) at temperature $30.0 \pm 0.5^\circ\text{C}$ and at different pH. The adsorption of Zn(II) by MSB increased nearly 11% against USB. Thus, chemical modification was found to be an effective source for promoting the efficiency of an adsorbent. Alkaline pH (above 7.0) inhibited adsorption of Zn (II). It might be due to either availability of small number sites in adsorbents or due to formation of hydrozinkate or zinakate ions. Thus, more adsorption of Zn (II) by chemically modified adsorbents sugarcane bagasse might be due to increase in surface area and chemical modification..

KEYWORDS: Heavy Metals, Sugar Cane Bagasse, Adsorption

Heavy metals released into the environment by various activities tend to persist indefinitely because of their non-biodegradable nature. These metals once discharged into the waste streams, get accumulated throughout the food chain, thus becoming a serious threat to the environment and adversely affecting the health of the people. Metal ions present in the waste water are characterized by their mobility in the liquid phase of ecosystem and by their toxicity to higher life forms even at low concentration. Hence, the removal of toxic and heavy metal contaminants from waste water is one of the most important environmental and economic issues today (R.K. Shrivastava *et al.*, 2002). Zinc (Zn^{2+}) one of the heavy metals in priority pollutants list of U.S. Environmental Protection Agency (USEPA) has been indicated in serious poisoning cases. It causes dehydration, electrolyte imbalance, stomach ache, nausea, dizziness and muscular incoordination (NRC, 1997). It is used in dry batteries, construction materials, pigment and painting process. It is widely used in coating iron and other metals in wood preservatives, photographic paper, accelerators for rubber vulcanization, ceramics, textiles, pigments etc (WHO, 1984).

A number of physico-chemical methods have been developed for the removal of toxic metal ions from aqueous solution (Dobson and Burgess 2007). Biological waste water treatment systems are chiefly designed for the removal of organic matter by activated sludge micro-organisms and the removal of heavy metals in these systems may be regarded as a side benefit. Nowadays efforts have been made to use cheap and available agricultural waste/natural products such as sugarcane bagasse, coconut shell, orange peel, rice-husk, maize cob,

etc. adsorbents remove heavy metals from waste water (Patil kishor *et al.* 2012; Bernard *et al.* 2013).

Several workers have reported on the potential use of agricultural by products as a good substrate for removal of metal ions from aqueous solutions and waste water. Chemical modification of agricultural adsorbents increase the sorption capacity of adsorbents there by increasing the efficiency of adsorbents (Ajmal *et al.*, 2000, Balaji *et al.*, 2014). This paper reports on the study of the kinetics of adsorption (K_1) at different pH. The role of pH in Zn (II) adsorption from aqueous solution in order to find out an appropriate pH range for maximum efficiency by using sugarcane bagasse under chemically modified and unmodified condition.

EXPERIMENTAL METHODS

Chemical used by analytical grade. Diluted HNO_3 was used for dissolution of Zn. Different concentration were prepared by serial dilution of stock solution by using distilled water. pH of the medium was adjusted by using 0.1 N NaOH or HCl, temperature, particle size and concentration of adsorbent was kept constant at different selected pH. Zn concentration was determined by using spectrophotometer following APHA method.

Adsorbent Preparation

The agricultural byproducts as sugarcane bagasse was collected from local farmers and soaked in hot deionized water and detergent for 24hrs. It was in hot deionized water to remove all debris and air dried. Air dried fiber was ground and sieved through a set of sieves to select the particle size.

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Adsorbent Activation

Selected fiber adsorbent was further soaked in 0.3M HNO₃ solution for 24 hrs and filtered through whatman No. 41 filter paper and rinsed with deionized water. The rinsed adsorbent was later air dried for 12hrs. A known amount of activated sugarcane bagasse was divided into two equal parts. One part was untreated and labeled USB (unmodified sugarcane bagasse) and second part was treated with 1M mercapto acetic acid (HS CH₂.COOH) solution and suspension was stringed for 30 min and labeled as MSB (modified sugarcane bagasse) labeled mixtures were filtered and residues of each filter paper was then soaked in 1M hydroxyl amine (NH₂OH) and filtered through filter paper. It was rinsed with distilled deionized water and washed residues were stored in airtight plastic container.

Kinetics of Metal Sorption

Kinetics of metal sorption studies of Zn(II) were carried out for each adsorbent at different pH and at temperature 30.0±0.5°C. The initial concentration of metal ion solution was 1.80×10⁻⁴M and particle size of the adsorbent was <55 M. A known amount solution (100ml) was taken in 250ml Erlenmeyer flask. Adsorbent (0.5 gm each) was soaked separately in flask and agitated in a shaker for a fixed time and constant speed (90 rpm). After the agitation for an equilibrium period the supernatant solution was filtered through whatman filter No. 41 and uptake was determined spectrophotometrically by using filtrate. Adsorption dynamics was calculated by taking adsorption rate constant. First order reversible reaction kinetics was used for the rate of reaction (Singh, A.K. *et al.*, 1987).

RESULTS AND DISCUSSION

The influence of pH of the metal ions solution on sorption of Zinc (II) a agricultural wastes. The adsorption of Zn (II) by agricultural waste as sugarcane bagasse (chemically modified and unmodified) is presented in Fig.1 and Fig. 2. The change in pH of the solution has no effect on the basic nature of the time growth adsorption curves and period of saturation. The time growth adsorption of Zn (II) by two adsorbents suggested that the removal was initially rapid and finally became constant due to the slow removal near saturation. The variation in percent adsorption at different pH by each adsorbent was studied.

The adsorption of Zn (II) increased from 23.0% to 64.0% and 34% to 75% in pH range of 5.5 to 8.5 with high

percentage at pH 7.5 by chemically unmodified and modified sugarcane bagasse respectively (Fig. 1 & 2). Above pH 7.5 the adsorption was decreased from 64.0% to 40.40% by unmodified bagasse and from 75.0% to 58.0% by modified bagasse at pH 7.5.

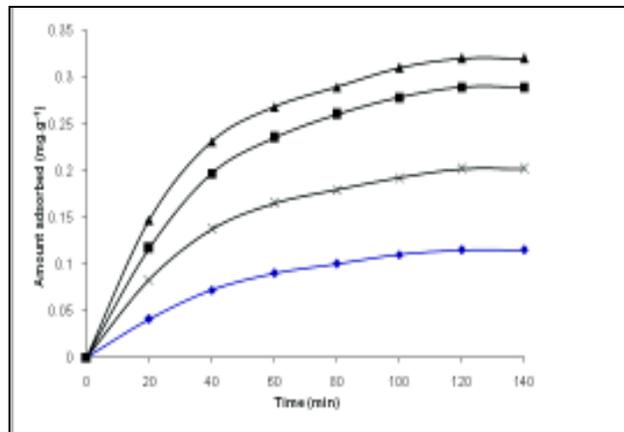


Figure 1: Time variation of adsorption of Zn(II) on unmodified sugarcane bagasse at different pH (Concentration 1.80×10⁻⁴M; Particle size < 55 M; Temperature 30.0±0.5°C)

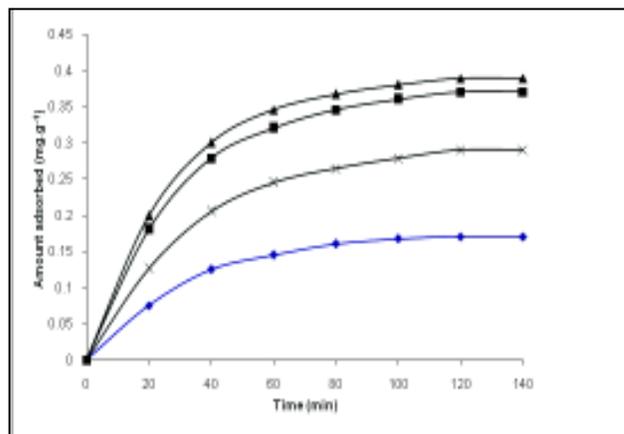


Figure 2: Time variation of adsorption of Zn(II) on modified sugarcane bagasse at different pH (Concentration 1.80×10⁻⁴M; Particle size < 55 M; Temperature 30.0±0.5°C)

Thus modified sugarcane bagasse was found more efficient than unmodified bagasse and maximum uptake was adsorbed at pH = 7.5, might be due to increase in surface area. It has been reported that surface area has a great effect on the sorption capacities of adsorbents (Abia and Asuque, 2006). Over all rate constant (k^1) and rate constant of adsorption k^1 and rate constant of adsorption k^1 at different pH for both adsorbent (unmodified bagasse and

as in Fig. 3 & 4. It is obvious from the results that pH of the medium affected these rate constants in accordance with the extent of adsorption.

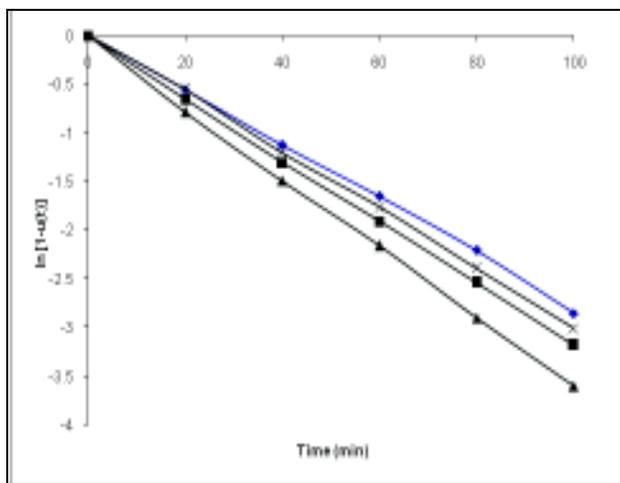


Figure 3: Rate constant plot for adsorption of Zn(II) on (modified) sugarcane bagasse at different pH

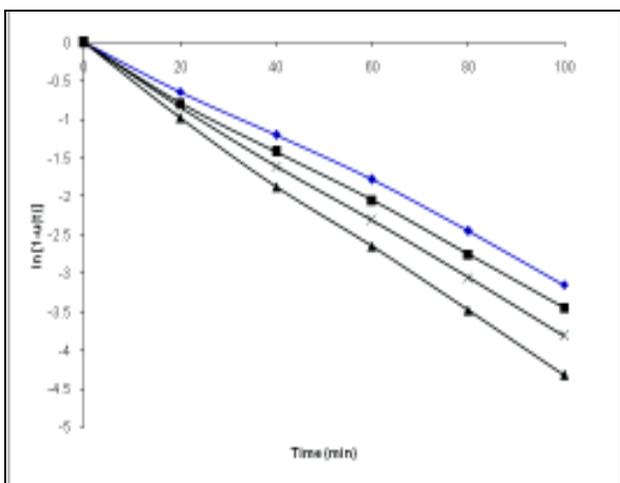


Figure 4: Rate constant plot for adsorption of Zn(II) on sugarcane bagasse (unmodified) at different pH

The variation in cation adsorption may be explained on the basis of surface hydroxylation, presence of oxides at solid solution interface in adsorbents (Ajay Kumar et al., 2009 & Balaji et al., 2014). Increase in adsorption above 7.5 might be due to availability of small number sites in both cases for adsorption as reported earlier for the adsorption of Zn(II) by silica (Pandey *et al.*, 1985). At higher pH formation of hydrozinkate and zinkate ions cannot be ruled out (Singh *et al.*, 1988). Thus more adsorption of Zn (II) by chemically modified adsorbents

area of adsorbents which increased with chemical modification and has a great effect on the sorption capacities of adsorbents. So, the use of low cost adsorbents but not only can also minimize cost inefficiency contribute to the sustainability of the surrounding environment.

CONCLUSION

The adsorption of Zn(II) chemical kinetics was rapid in the initial stage followed by slow rate of adsorption. The experimental results showed that under optimized conditions modified sugarcane bagasse can be used as a better adsorbent for the removal of Zn (II) in alkaline medium which may be quite useful to develop an appropriate technology for designing waste water treatment, using unconventional adsorbents by adjusting pH of the solution for the removal of pollutants with maximum efficiency.

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