

A Novel Method for the Removal of Zinc(II) by Natural Clay Available in a Pond in Tiruchirappalli, India

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Abstract—The removal of Zn^{2+} ions in aqueous solution was investigated by adsorption process on natural pond clay. In this study, the effect of pH, adsorbent size, adsorption size, initial concentration of metal ion, adsorbent dose on the sorption capacities were carried out.. Adsorption isotherm models were studied. According to the results, natural clay is recommended as cheap and efficient adsorbent for the removal of zinc- ions from industrial waste water.

Key words: Zinc ion, adsorption, Freundlich, Langmuir.

I. INTRODUCTION

Cadmium, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters, which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries, etc[1]. Consuming large amounts of zinc, even for a short time, can cause stomach cramps, nausea, and vomiting. The proposed limit of zinc in drinking water is 5 ppm as proposed by FDA [2]. The search for new technologies involving the removal of toxic metals from wastewaters has attracted attention to adsorption[3]. Apart from environmental issues, technological aspects of metal recovery from industrial water must also be considered [4]. In the present research work, natural clay is used as the sorbent to remove $Zn(II)$ ions from aqueous solution and its isotherm models were studied.

II. EXPERIMENTAL

Natural clay (~500g) from a pond in Tiruchirappalli (~one foot from the surface – during June 2013) was collected, washed well with water (to remove the soluble impurities) and filtered. Then, the material was stirred well with ~1N HNO_3 (to remove the acid – soluble impurities), filtered and washed repeatedly with distilled water (filtrate checked with litmus paper) dried, sieved to different sizes and kept in airtight glass containers.

III. BATCH EQUILIBRATION METHOD

All experiments were carried out in batch mode. Batch mode was selected because of its simplicity and reliability.

In many applications the preliminary evaluation program may take the form of a simple feasibility study where capacities of adsorbents for the removal of chosen adsorbates are determined by simple batch experiments in laboratory. This study together with the knowledge of similar operating systems may provide sufficient capacity and design information to proceed with full scale design. In other cases considerable effort may be required for full scale implementation.

Keeping this in view, batch experiments were done in different ground joint glass bottles of 100 ml capacity. Prior to each experiment, a predetermined amount of adsorbent was added to each flask. The shaking was kept constant (100 rpm) for each run throughout the experiment to ensure equal mixing. Each bottle was filled with 50 ml of sample before commencing stirring. The flask containing the sample was withdrawn from the shaker at the predetermined time interval, filtered and the residual concentration of the sample was measured. Concentration of metal ions before and after adsorption was measured using a photo colorimeter ($\lambda = 545nm$). Concentration of metal ions before and after adsorption was measured using a photo colorimeter.

The metal ion retained in the adsorbent phase, q_e (mg/g) was calculated using [5]

$$q_e = \frac{(C_i - C_e)}{m} V$$

Where V = Volume (ml) of the equilibrated solution,
 m = Mass of the adsorbent (g),
 C_i = Initial concentration of synthetic Zn^{2+} solution (mg/l),
 C_e = Zn^{2+} at equilibrium (mg/l).

The percentage removal (%) of Zn^{2+} ions was calculated using the following equation,

$$\text{Removal (\%)} = \frac{(C_i - C_e)}{C_i} \times 100$$

IV. EFFECT OF VARIATION OF PH

For Zinc, % removal was high at pH 6 for natural clay. It is clear that, the percent removal decreases with further increase in pH value. The decrease in percent removal may be attributed to the formation of zinc hydroxide precipitate [6].

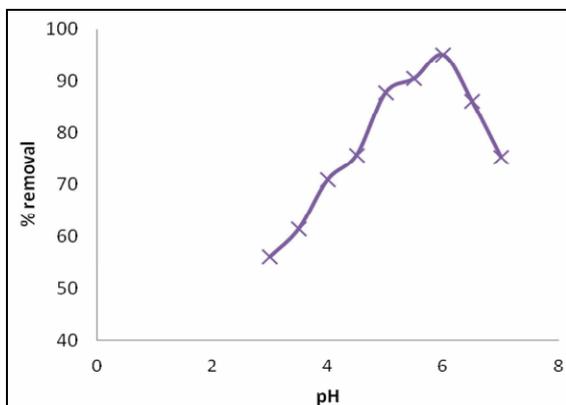


Fig. 1 Variation in % removal of Zn(II) with pH

V. EFFECT OF VARIATION OF ADSORBENT SIZE

Larger surface area implies a greater adsorption capacity, for example, carbon and activated carbon. Smaller particle sizes reduce internal diffusion and mass transfer limitation to penetrate of the adsorbate inside the adsorbent (i.e., equilibrium is more easily achieved and nearly full adsorption capability can be attained). Fig. 2 represents the removal efficiency of zinc by natural clay through seven different particle sizes (< 75 μm , 75 μm -150 μm , 150 μm -250 μm , 250 μm -300 μm , 300 μm -355 μm , 355 μm -425 μm and 425 μm -500 μm). It can be observed that the maximum adsorption efficiency is achieved with < 75 μm for zinc by natural clay. In the present case, there is a decrease in adsorption efficiency for larger particle size. This may due to the lack of availability of the adsorption sites. In maximum cases, lower particle size showed maximum adsorption which may due to the availability of larger surface area [7].

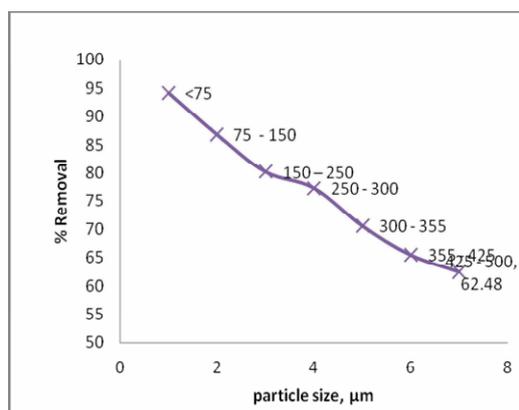


Fig. 2 Variation in % removal of Zn(II) with adsorbent size

VI. EFFECT OF VARIATION OF CONCENTRATION OF METAL ION

Fig. 3 shows that adsorption capacity increasing as the metal concentration increases from 25 to 200 mg/l. The trend is that of the result of the progressive increase in the electrostatic interaction between the ions and the adsorbent active sites. Moreover, this can be by the fact that more adsorption sites were being covered as the metal ions concentration increases [8]. Besides, higher initial concentrations lead to an increase in the affinity of the ions towards the active sites [9]. The decline in the adsorption capacity is due to the availability of smaller number of surface sites on the adsorbent for a relatively larger number of adsorbing species at higher concentrations [10].

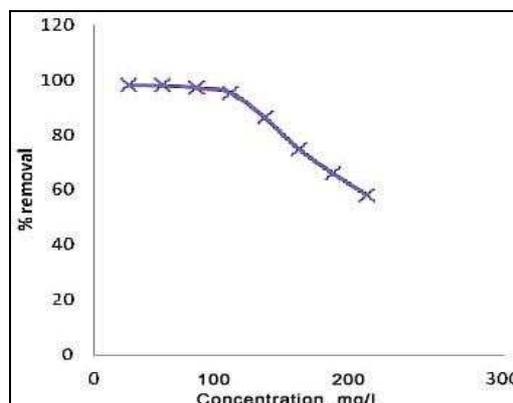


Fig. 3 Variation in % removal of Zn(II) with concentration

VII. EFFECT OF VARIATION OF CONTACT TIME

The relationship of percentage metals removal by adsorbent with contact time was plotted and presented in Fig. 4. The percentage metal removal approached equilibrium within, 30 min for adsorption of zinc by natural clay. The fast adsorption was probably due to the initial concentration gradient between the adsorbate in solution and the number of vacant sites available on the surface of the adsorbent at the beginning. The progressive increase in adsorption and consequently the attainment of equilibrium adsorption may be due to limited mass transfer of the adsorbate molecules from the bulk liquid to the external surface of adsorbents.

It was noted that the sorption capacities corresponding to equilibrium varied for each metal [11].

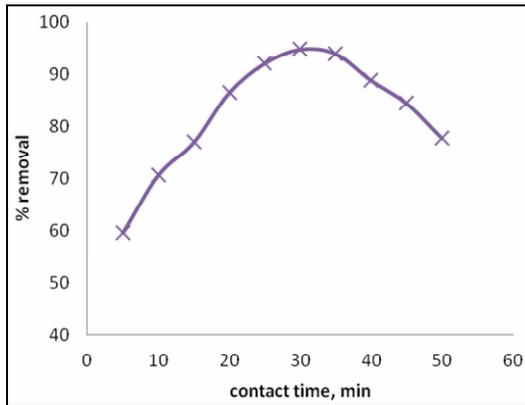


Fig. 4 Variation in % removal of Zn(II) with contact time

VIII. EFFECT OF VARIATION OF DOSE OF ADSORBENT

The effect of variation of dosage on amount of metal adsorbed is shown in Fig-5. The initial increment in adsorption capacity with increase in adsorbent dosage was expected, since number of adsorbent particles increases and thus more surface areas were available for metals attachment. The present study reveals that as the adsorbent dose was increased from 0.25 g to 2.25 g there was increase in the adsorption of metal ions on to the surface of the adsorbents [12].

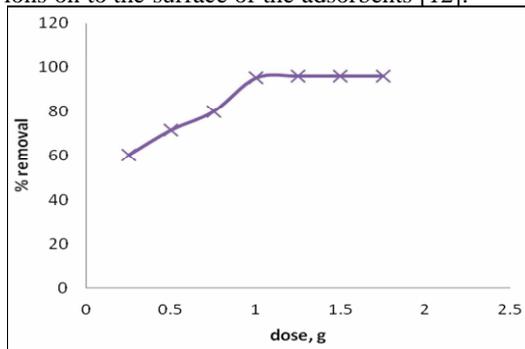


Fig. 5 Variation in % removal of Zn(II) with dose of adsorbent

IX. EFFECT OF VARIATION OF TEMPERATURE

In the present work, the effect of temperature on the sorption of Zinc from single metal ion solution using the adsorbent natural clay in the temperature range of 27-47°C. With increasing temperature, the attractive forces between biomass surface and metal ions are weakened and the sorption decreases.

Careful examination of the figure revealed that most of the metal ions were removed between the temperatures of 32 to 37°C. At high temperature, the thickness of the boundary layer decreases, due to the increased tendency of the metal ion to escape from the biomass surface to the solution phase, which results in a decrease in adsorption as temperature increases. The decrease in adsorption with increasing temperature, suggest weak adsorption interaction between biomass surface and the metal ion, which supports physisorption.

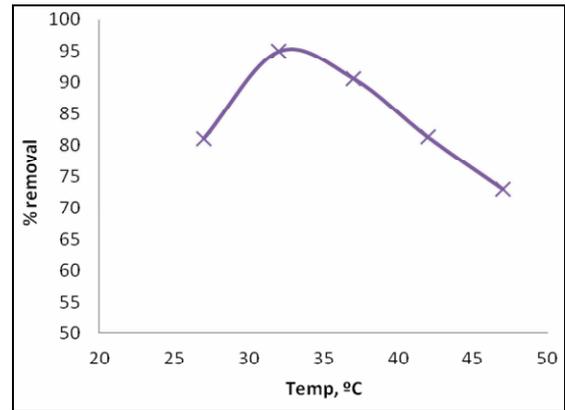


Fig. 6 Variation in % removal of Zn(II) with temperature

A. Adsorption Isotherms

The adsorption isotherms [13, 14] are studied using initial concentration of Zn(II) between 25 and 200 mg/L at an adsorbent dose of 1 gm/L. The data obtained is fitted into the Langmuir adsorption isotherm which is the most popular and is a two-parameter equation described as:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e}$$

Where,

- C_e = the equilibrium concentration of adsorbate (mg/l)
- q_e = the amount of Iron ion adsorbed per gram of the adsorbent at equilibrium (mg/g)
- Q_0 = maximum monolayer coverage capacity (mg/g)
- K_L = Langmuir isotherm constant (l/g)

The linear nature of the plot shows that the adsorption follows the Langmuir isotherm. The adsorption data obtained are also fitted to the Freundlich isotherm which is the earliest known relationship known as described by the following equation

$$Q_e = K_f C_e^{\frac{1}{n}}$$

Where K_f = Freundlich isotherm constant
 n = adsorption intensity

- C_e = the equilibrium concentration of adsorbate
- Q_e = the amount of Fe²⁺ adsorbed per gram of the adsorbent at equilibrium

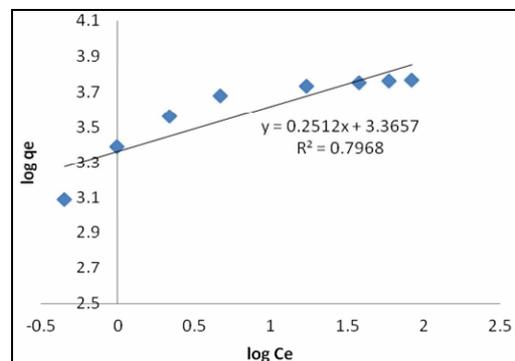


Fig. 7 Isotherm for Zn(II) ions removal by pond clay

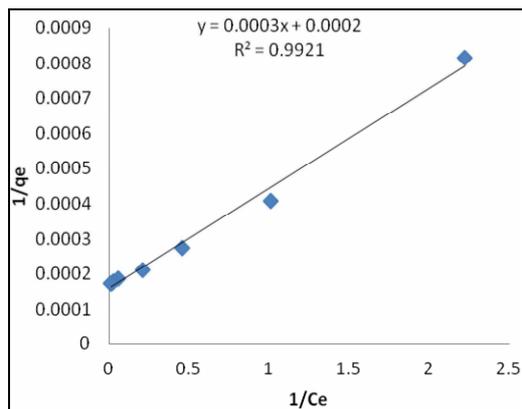


Fig. 8 Isotherm for Zn (II) ions removal by sand

The data fitted well for Langmuir adsorption isotherm which confirms the formation of monolayer adsorption.

X. CONCLUSION

Natural clay, a cheap and easily available material can be used as an effective adsorbent for removing zinc(II) ions from the waste water. The optimum conditions of pH, adsorbent size, initial concentration of metal ion, adsorbent dose on the sorption capacities were studied. The application of adsorption model viz., Langmuir and Freundlich was done. The data obtained confirmed the application of natural clay as a effective adsorbent on the removal of zinc ions.

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