Adsorption of Zinc from Zinc Acetate Solution on Clay (Kaolinite)

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Summary: Adsorption studies of Zinc from Zinc acetate solutions on Clay (Kaolinite) were made under varying conditions of time and pH. Adsorption equilibrium was found to be established within two hours in case of Zinc acetate solution of 50 ppm concentration. Increase in pH was found to have a significant positive effect on the extent of adsorption. Freundlich's and Langmuir's equations, when applied to the isotherm data, obeyed very well.

Introduction

Generally, "Clays are more or less hydrated aluminum silicates with appreciable amounts (quantities) of iron, alkalies and alkaline earth metals" [1]. The structure of Kaolinite (China Clay) is composed of a single tetrahedral sheet and a single alumina octahedral sheet combined in a unit. So, that the tips of the silica tetrahedrons and one of the layers of the octahedral sheet form a common layer. All the tips of silica tetrahedrons point in the same direction and toward the centre of the unit made of the silica and octahedral sheets [2]. In a Kaolinite crystal, essential components are large anions of oxygen and hydroxyl unit held together by much smaller cations. As the negatively charged ions (anions) are very much larger than the positively charged ones (cations), the former predominate in the external layer. The net result of this is that the surface of clay particles become negatively charged when suspended in a water medium. By virtue of their negative surface charge, Clay particles have the capacity to attract and adsorb cations from the surrounding suspension. In general the greater the charge and higher the atomic weight of the cation, the more readily will it be adsorbed [2].

Clays are widely used for various purposes, e.g. for manufacture of various ceramics articals, for decolorization of various organic and inorganic substances, and for different adsorption processes etc. Due to their great adsorption capability, Clays act as a good adsorbent for the removal of undesirable substance from the edible oil as well as from fuel oil [3]. Clays can also be used for the removal of toxic materials present in waste radioactive water [4] , for the clarification of sugar-cane juice in sugar industry [5], for deinking old news print paper [6-8] etc.

Earlier investigations reported that Clays have great adsorption capacity for different organic as well as inorganic compounds and the adsorption of these compounds on Clays is influenced by various factors, such as contact time [9], solution concentration [4,9] and pH [10-11]. The present work was therefore undertaken with a view to investigate the adsorption characteristics of China Clay for adsorption of Zinc from Zinc acetate solution and also to avoid the undesirable properties of carbon blacks and activated carbon encountered in some adsorption processes. The effect of time, concentration, and pH of salt solution on the extent of adsorption, employing continuous stirring of the suspension were also investigated in the current study.

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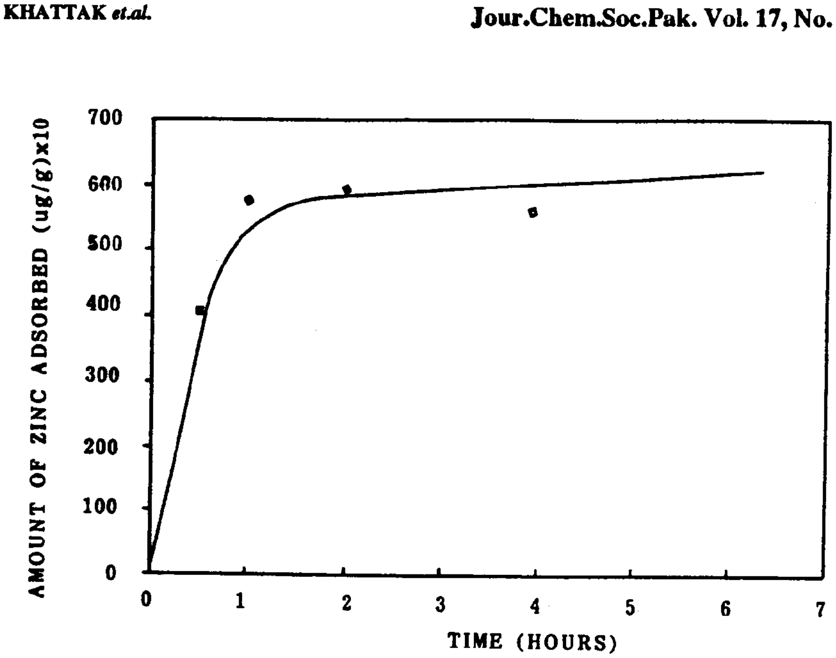

Fig.1: Adsortpion of Zinc from Zinc acetate solution at different duration: Clay dosage: 0.5 grams; concentration of Zinc: 50 ppm, pH = 4-5.

Results and Discussion

Surface area of the clay used in current study was determined by Snow's iodine adsorption method [13]. Average surface area of the Clay used was 81.01 m^2/cg^3 showing small amount of microporosity.

Equilibration time for adsorption of Zinc from Zinc acetate solution was determined and is given in Figure 1, which shows that equilibrium was established within two hours. Therefore, two hours stirring time was used through out for the adsorption isotherm study.

Effect of pH on adsorption of Clay was determined by stirring different concentration of zinc acetate solution (10-100 $\mu g/cm^3$) with 0.5 grams of Clay for two hours at 35°C. The experiment was performed for three different pH ranges i.e., 2-3, 4-5, and 6-7 under similar experimental conditions. Results are shown in Figure 2, which shows that amount of Zinc adsorbed increases as the pH of the Zinc salt solution increased, Fig. 2 shows that adsorption of zinc is less at low pH range 2-3 and higher at higher pH range 6-7 (without blank correction) and with blank correction. The figure also shows that when the adsorption is corrected for blank at pH 6-7 to avoid precipitation effect of Zinc, the amount of Zinc adsorbed was still high as compared to other pH ranges. At higher pH range predominant precipitation occur which may be of $Zn(OH)_2$ precipitate and higher amount of Zinc adsorbed become low in case of blank correction, which might be due to reduction of the Zinc concentration in the solution. The lower adsorption of Zinc at low pH range (2-3) may be attributed to that, the Clay contain large fraction of negatively charged ions (anions) on its surface as compared to cations [2], which can attract the positive H^+ ions of medium resulting in reduction of active adsorption sites, which in turn reduces the adsorption of cation (Zn^{++}), whereas at high pH range 6-7, the active adsorption sites are fully available to cation (Zn^{++}) resulting greater adsorption of Zn^{++} at that pH range. Moreover, there is less solubility of Zinc salt at high pH range and high solubility at low pH range which may also contribute to the adsorption process, i.e low solubility favour adsorption, resulting in greater adsorption of Zinc at high pH and vice versa.

Freundlich equation [$\ln(x/m) = \ln k + 1/n \ln C$] was applied to the results of Fig. 2, where x is the amount of solute adsorbed, m is the amount of adsorbent, C is the equilibrium concentration, 1/n is the slope. Results obtained by the application of Freundlich equation are shown in Fig. 3. The results show that all adsorption isotherms obey Freundlich equation. The values of adsorption

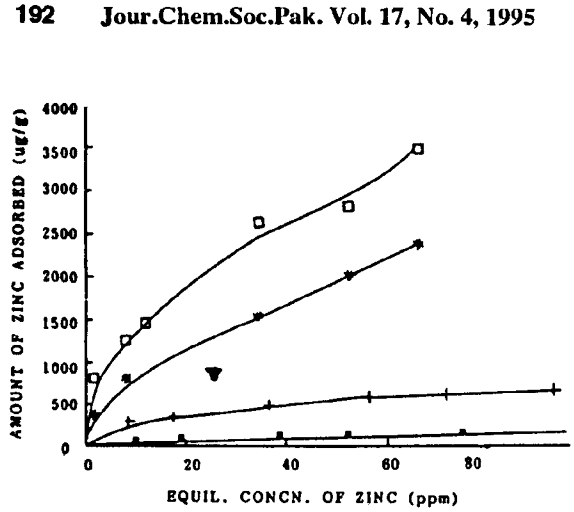

Fig.2: Adsorption Isotherm of Zinc from Zinc acetate solution at different pH ranges: Clay dosage: 0.5 grams, concentration of Zinc: 10-100 ppm, pH range:•, 2-3; +, 4-5; *, 6-7 (with blank correaction), □ 6-7(without blank correaction).

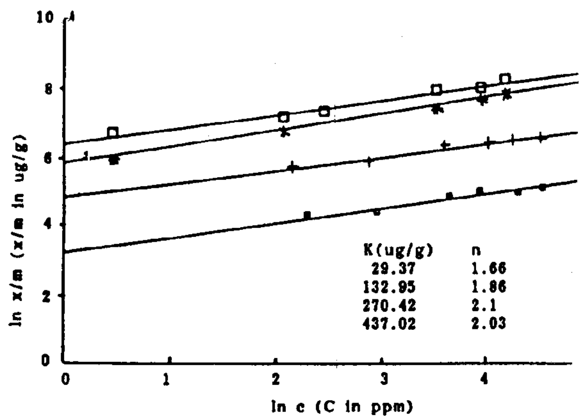

Fig.3: Freundlich's Isotherms of Zinc from Zinc acetate soltuion at different pH ranges: Clay dosage: 0.5 grams, concentration of Zinc 10-100 ppm; pH ranges:•, 2-3; + 4-5; *, 6-7 (with blank correction); □, 6-7 (without blank correction).

capacities k increases as the pH range increases which have the values 29.37 μg/gm, 132.95 μg/gm, 270.42 μg/gm and 437.02 μg/gm at pH 2-3, 4-5 and 6-7 (with and without blank correction) respectively. Low adsorption capacity at low pH range 2-3 might be due to high solubility of Zinc acetate salt and also competition between H^+ and Zn^{++} ions towards active adsorption sites.

The linearised form of Langmuir's equation C/(x/m) = 1/ab + C/b was also applied to the results of the Figure 3, where x/m is the amount of solute adsorbed per gram of adsorbent, C is the equilibrium concentration of solution, b is the amount of solute adsorbed per gram of adsorbent, a is proportional to the heat of adsorption and temperature. Results obtained by the application of Langmuir's equation are shown in Fig. 4. The Fig. 4 shows a linearised form, indicate that results obey Langmuir equation similar to Freundlich equation. When C/(x/m) is plotted Vs C, a straight line with slope 1/b and intercept 1/ab is obtained. The values of b are 198.01 μg/gm, 796.81 μg/gm, 2573.33 μg/gm and 8000 μg/gm at pH range 2-3, 4-5 and 6-7 (with and without blank correction) respectively which shows that monolayer adsorption of the Clay used increases as the pH increases, as indicated from their values of b.

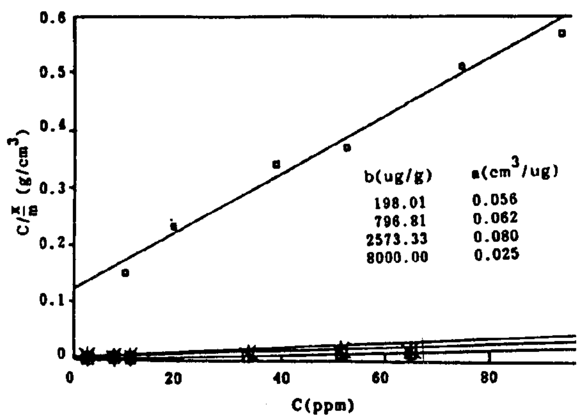

Fig.4: Langmuir;s Isotherms of Zinc for Zinc acetate solution at different pH ranges: Clay dosage 0;5 grams; conc. of zinc : 10-100; pH ranges: , 2-3; + 4-5; *, 6-7 (with blank correction; □, 6-7 (without blank correction).

Experimental

Determination of surface area

Surface area of the Clay used (CC-31 China Clay) was determined by C.W. Snow's Iodine adsorption method [12] as follow.

Preparation of iodine solution

Iodine solution was prepared by dissolving 142.50 g Potassium Iodide and 15.0 g Iodine in distilled water. The solution was then diluted to 250 ml with distilled water.

Procedure

Five ml of iodine solution was added to one gram of clay contained in iodine flask and was allowed to stand for two hours. To the flask 45 ml of distilled water was added and the flask was swirrled gently for one minute and was then allowed to stand for one hour. Twenty ml from the top supernant solution was taken and titrated with 0.0394 N sodium thiosulphate solution using starch as indicator. The surface area in square meter per gram was then calculated as 12.5 x (24 - V), where V is the volume of sodium thiosulphate in ml required to titrate a 20 ml of the iodine solution withdrawn from iodine flask. Each determination was done in triplicate.

Determination of equilibration time of adsorption of Zinc on Clay

The equilibration time of adsorption of Zinc from Zinc acetate solution on Clay (CC-31 China clay) was determined by taking 0.5 grams sample of Clay in conical flask then 50 cm^3 of 50 $\mu g/cm^3$ of Zinc acetate solution was transferred into conical flasks through a 50 cm^3 pipette. The flasks were placed on water bath over a magnetic stirrer at 35°C for different duration of time. The pH was measured before and after stirring with a pH meter. The contents were then filtered and first 5 cm^3 of the filtrate were discarded. Measured volume of the filtrates were titrated against 0.001M E.D.T.A. (Ethylene diamine tetra acetic acid) solution using E.B.T. (Erichrome Black-T) as an indicator. Blank determinations were performed similarly. The amount of Zinc adsorbed per gram of Clay at different duration of time was calculated as follows:

$$\text{Apparent adsorptionin } \mu g/gram = \frac{V_1 - V_2 \times M \times \text{Atomic weight of Zinc} \times 1000}{\text{Weight of Clay taken in grams}}$$

M = Molarity of E.D.T.A. = 0.001 M Depending on standardization.

V_1 = Volume of E.D.T.A. solution used for 50 cm^3 blank zinc salt solution.

V_2 = Volume of E.D.T.A. solution used for 50 cm^3 zinc salt solution containing clay sample.

Determination of adsorption isotherm of zinc on Clay

Zinc acetate solution of different concentration (10,20,40,60,80,100 $\mu g/cm^3$) were prepa-red. Then, 50 cm^3 solution of each concentration was transferred to six tidy conical flasks containing 0.5 gram Clay with the aid of 50 cm^3 pipette. Then flasks were firmly closed by means of stopper and were put over water baths placed on magnetic stirrers at a temperature 35°C. Sitirring were continued for a period of two hours. After stirring, the slurries were filtered, pH were measured before and after stirring. Clear filtrates were then titrated against 0.001M E.D.T.A. in the presence of an indicator and 0.25 cm^3 buffer solution (pH-10). End point was noted as the colour changed from violet to blue. Blank determinations were also performed under similar experimental conditions.

Determination of the effect of pH on adsorption isotherm on Clay

For the determination of pH effect on adsorption isotherm, 0.1N NaOH solution were prepared. Zince salt solution of concentration ranging from 10 ppm to 100 ppm were also prepared. pH of Zinc salt solution was adjusted in the range 6-7 by gradual addition of some drops of 0.1N NaOH solution. The determination of adsorption isotherm at pH range 6-7 was also performed under similar experimental conditions as were used for determination of adsorption isotherm at pH range 4-5. Blank determination were also performed for each concenration. pH of Zinc salt solution was also adjusted in the range of 2-3 by gradual addition of 0.1N HCl. Same procedure was also adopted at this pH range for the determination of adsorption isotherm. Blank determinations were also performed for each concentration. Each determination was done in triplicate.

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