

## Spectroscopic studies and kinetic modeling of a modified soil adsorbent

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### Abstract

One of the most favorable techniques of wastewater treatment has been adsorption. Hence, soil was modified so as to get a promising adsorbent with salient features, including enhanced adsorption efficiency and favorable kinetics. The adsorbent was studied with FTIR (Fourier transform Infrared spectroscopy), SEM (Scanning electron microscope) and EDX (Energy Dispersive X-Ray Analyzer) so as to understand the characteristics of the adsorbent. It was observed that the adsorption followed Langmuir's isotherm and pseudo-second order kinetic models. At the optimum pH of 8, the saturation level of adsorption, of 78.5 mg g<sup>-1</sup> of Zn<sup>2+</sup>, was reached within 20 min.

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## 1. Introduction

The increasing instances of discharge of heavy metals into streams, lakes, rivers and groundwater have become a major concern. The non-degradable heavy metals have a tendency to bio-accumulate in living organisms, whereby causing toxicity [1, 2]. The presence of zinc in high concentration ( $> 4$  mg/L) [3] may have negative impact on the human health. The major anthropogenic sources of zinc are industries associated with galvanization, fertilizers, pesticides, pigments and polymer stabilizers [4, 5]. Hence, the removal of these heavy metals from the contaminated water, before it reaches human consumption, is very crucial. Therefore, many removal methods, including co-precipitation, membrane filtration, adsorption etc., have been proposed and accomplished [6, 7]. However, adsorption promises an efficient, economical and flexible method of removal of heavy metals. It is well known that minerals, present in the soil, behave as a sink for heavy metals and thus influences its mobility and distribution [8,9]. Hence, attempts have been made to mimic the natural adsorbents (of heavy metals) by developing new adsorbent with higher potential to adsorb heavy metals [10]. There has been many reports emphasizing metal oxides as significant factor of metal adsorption [11, 12] while on the other hand, soil can play a significant role as an adsorbent of heavy metals by virtue of its varying constituent phases (such as clay minerals, carbonates, organic matter, and metal oxides) [13]. Here we have attempted to combine the scavenging/or adsorbing property of both a chelating agent and multi-component soil, so that the final adsorbent would be efficient in the treatment of wastewater (especially those laden with heavy metals).

## 2. Materials and methods

### 2.1. Instruments and equipments

Flame atomic absorption spectrometry (Agilent, USA) and a pH meter (GONDO Electronic Co. Ltd., Taiwan) were respectively employed for the determination of the concentration of  $\text{Zn}^{2+}$  and the pH of the solutions. All the equilibrium studies were conducted with a heating cum magnetic stirrer (Benchmark Scientific, USA). The samples and products were dried in a heating oven (BINDER GmbH, Germany). The adsorbent was reduced to the desired sized particles by means of a stainless steel grinder and ASTM standard sieves.

### 2.2. Reagents and raw materials

The solutions of  $\text{Zn}^{2+}$  were prepared with  $\text{ZnSO}_4$  (Loba Chemie Pvt. Ltd., India). Soil was obtained from the local area and subsequently washed with water, dilute  $\text{HNO}_3$  and methanol. The soil was air dried before storing for further modification. Buffer solutions (compositions) were used as: pH 1-2 (0.2 M KCl + 0.2 M HCl), pH 3-5 (0.1 M  $\text{CH}_3\text{COOH}$  + 0.1 M  $\text{CH}_3\text{COONa}$ ), pH 6 (1.0 M  $\text{CH}_3\text{COOH}$  + 1.0 M NaOH), pH 8-10 ( $\text{NH}_4\text{Cl}$  +  $\text{NH}_4\text{OH}$ ) [14].

### 2.3. Preparation of adsorbent

The soil was added to a beaker containing a concentrated solution of EBT (Eriochrome Black T) prepared in a solvent system of  $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$ . The mixture/suspension was allowed to stand for a period of 24 hours (with intervening stirring). The so formed solid product was then decanted out from the mixture and then left, for drying, in an oven at  $60^\circ\text{C}$  until a constant weight was obtained.

### 2.4. General method for single batch

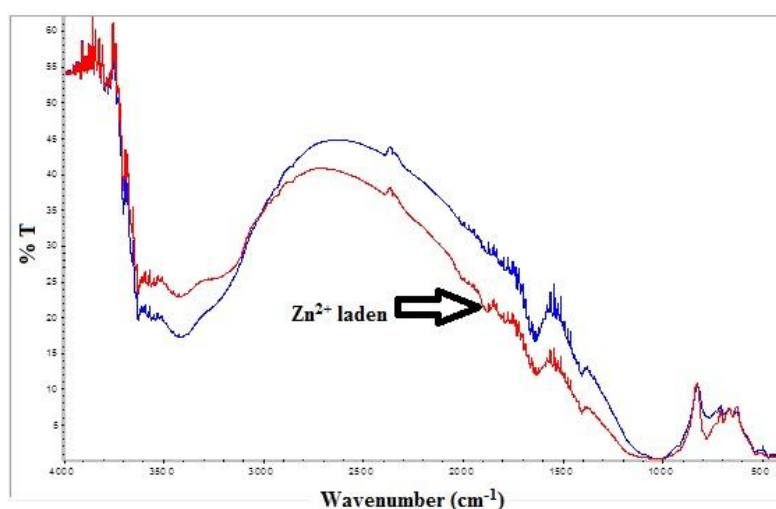
A weighed amount of adsorbent was taken in a beaker (equipped with a magnetic stirrer) and then a  $\text{Zn}^{2+}$  solution (standard) was added to it. The mixture was buffered to a pre-selected pH and then equilibrated for a definite time interval. After equilibration, the filtrate was subjected to FAAS. The amount of  $\text{Zn}^{2+}$  retained by the adsorbent was

calculated by using the following relation:  $q_e = (C_0 - C_e) \times \frac{V}{w}$ , where,  $q_e$ ,  $C_0$  and  $C_e$  represent the equilibrium adsorption capacity ( $\text{mg g}^{-1}$ ), the initial and the equilibrium concentration ( $\text{mg L}^{-1}$ ), respectively [15]. Again,  $V$  (L) and  $w$  (g) represent, respectively, the volume (of solution) and adsorbent's weight.

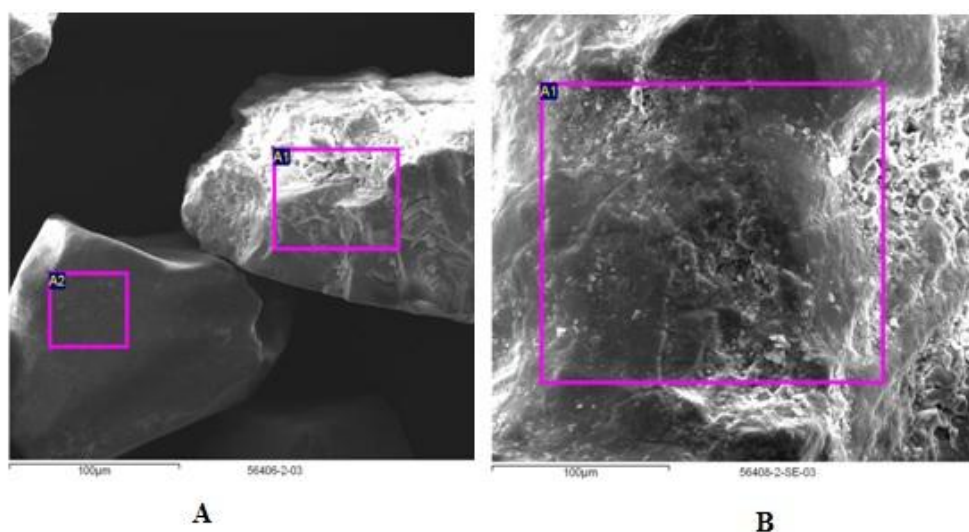
### 3. Results and Discussions

#### 3.1. FTIR spectrum and SEM-EDX studies

The FTIR spectra (Fig 1), of the modified soil, reveals the characteristic peaks of N=N and -OH at  $1513\text{--}1631\text{ cm}^{-1}$  and  $3409\text{--}3654\text{ cm}^{-1}$ , respectively [16]. However, on loading the adsorbent with  $\text{Zn}^{2+}$ , the -OH peaks undergoes shifts to  $3415\text{--}3623\text{ cm}^{-1}$ , while the peaks at  $1513$  and  $1530\text{ cm}^{-1}$  disappeared. These changes may be explained by assuming the involvement of these bonds in the retention of the  $\text{Zn}^{2+}$  metal ions (Fig. 1). The SEM report (Fig. 2) reveals the irregular deposition of the divalent metal ion ( $\text{Zn}^{2+}$ ), onto the modified soil matrix, which is also favored by the EDX report Fig 3a, 3b.



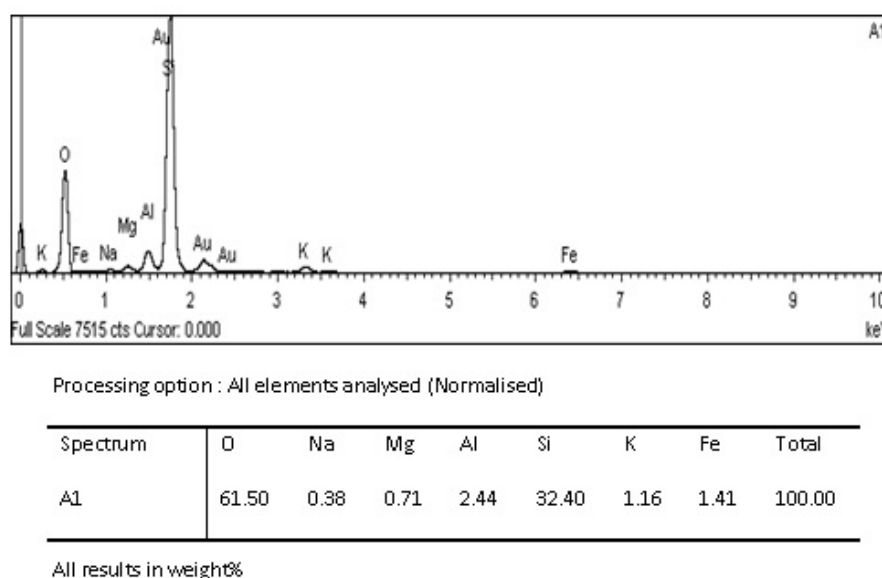
**Figure 1:** FTIR spectra of the adsorbent, before and after the adsorption of  $\text{Zn}^{2+}$ .



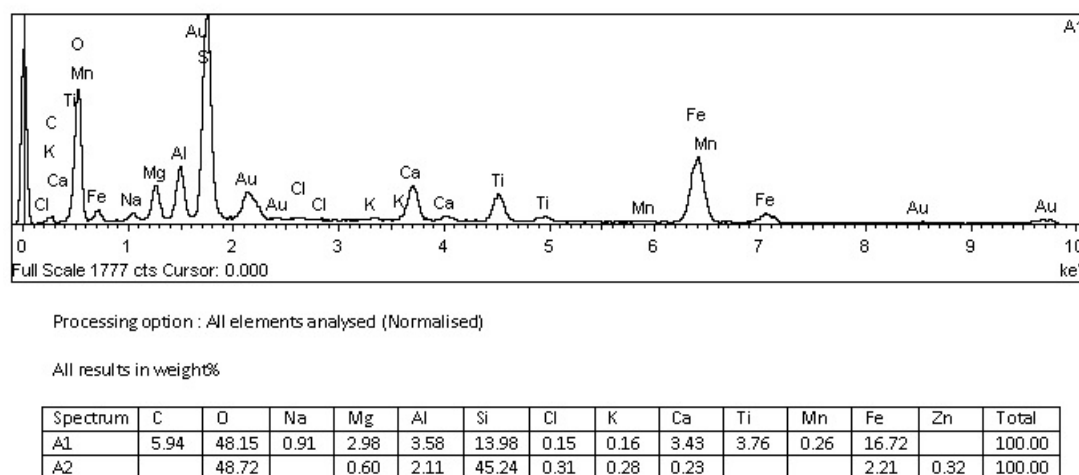
**Figure 2:** SEM of the adsorbent before (a) and after (b) the adsorption of  $\text{Zn}^{2+}$ .

### 3.2. Effect of pH

Each of the 6 batches, buffered at different pH (Fig. 4) was prepared by adding 50 mL of  $\text{Zn}^{2+}$  solution ( $5 \times 10^{-3} \text{ mol L}^{-1}$ ) into a beaker containing 0.1 g of adsorbent. It was observed that the adsorption capacity increased with increasing pH and the maximum was reached at pH 8.0. At high pH, the constituting hydroxyl groups gradually get deprotonated which renders it negatively charged. Hence, the positively charged  $\text{Zn}^{2+}$  finds its way, through the solution, into the solid phase where it gets involved in the formation of chelate-complex with the participating azo and the two hydroxyl groups (Fig. 4).



**Figure 3a:** EDX of adsorbent before the adsorption of  $\text{Zn}^{2+}$ .

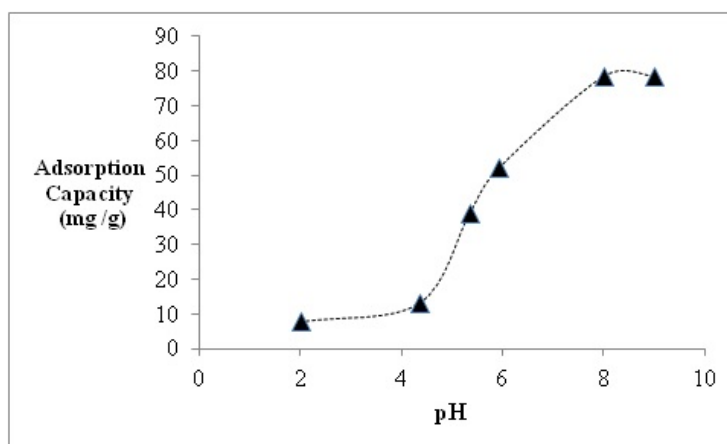


**Figure 3b:** EDX of the adsorbent after the adsorption of  $\text{Zn}^{2+}$ .

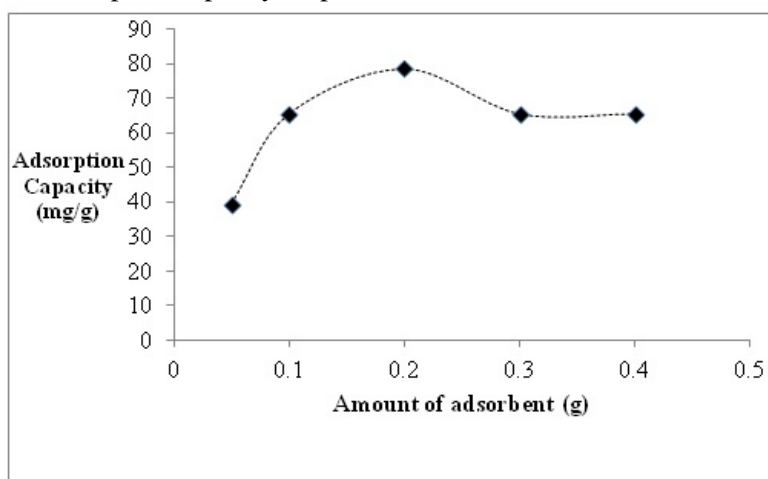
### 3.3. Effect of concentration and amount of adsorbent

For studying the effect of concentration, each of the 6 batches, buffered at pH 8.0, was prepared by adding varying concentration of  $\text{Zn}^{2+}$  solution into a beaker containing 0.1 g of the adsorbent. The same amount of adsorbent, containing a fixed number of active sites, gradually decreases its uptake (of the target metal), with the increasing initial concentration due to saturation. The adsorption capacity increased with increasing initial concentration (of  $\text{Zn}^{2+}$ ), for at least lower range of concentration. This behavior may be explained on the basis of concentration gradient between the

bulk solution and the surface of the adsorbent. At lower range of concentration, the concentration gradient overcomes the resistance of mass transfer through the solution up to the vicinity of the solid surface. Again, for determining the effect of amount of adsorbent, each of the 6 batches, buffered at 8.0 pH, was prepared by loading varying amount (Fig, 5) of the adsorbent into the 50 mL of  $\text{Zn}^{2+}$  solution ( $5 \times 10^{-3} \text{ mol L}^{-1}$ ) contained in a beaker. The increase in the amount of adsorbent enhanced the removal efficiency of the  $\text{Zn}^{2+}$  ions, but however, it was observed that the adsorption capacity reduced after 0.1 g. Such behavior may be explained by assuming that there is an availability of abundant binding sites, among which some are gradually left unoccupied.



**Figure 4:** Dependency of the adsorption capacity on pH.



**Figure 5:** Effect of the amount of adsorbent on the adsorption capacity.

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### 3.4. Kinetics of adsorption

Each of the 6 batches, buffered at 8.0 pH, was prepared by adding 50 mL of  $\text{Zn}^{2+}$  solution ( $5 \times 10^{-3} \text{ mol L}^{-1}$ ) into a beaker containing 0.1 g of the adsorbent. Each of the batches was equilibrated for different intervals of contact time ranging from 10 min to 40 min. It was observed that the adsorbent reaches its saturation level, of  $78.5 \text{ mg g}^{-1}$ , within 20 min of contact time (Fig 6). As claimed in previous studies [17], adsorption is often well represented by pseudo-second-order kinetic model (Fig. 6). Thus, if  $q_e$  and  $q_t$  represent the amount ( $\text{mg g}^{-1}$ ) of  $\text{Zn}^{2+}$  adsorbed, by the adsorbent, at equilibrium and at time “t”, respectively, then the pseudo-second-order kinetic equation:  $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$ , would be the most befitting with  $k_2$  as the rate constant ( $\text{g mg}^{-1} \text{ min}^{-1}$ ). Hence, the plot of  $q/q_t$  against  $t$  (contact time) was found to be linear with  $R^2$  well above 0.998. Such befitting nature would suggest that this

model correspond to the rate-controlling step, which would again indicate chemisorptions as the major route of adsorption [18].

### 3.5. Isotherm study

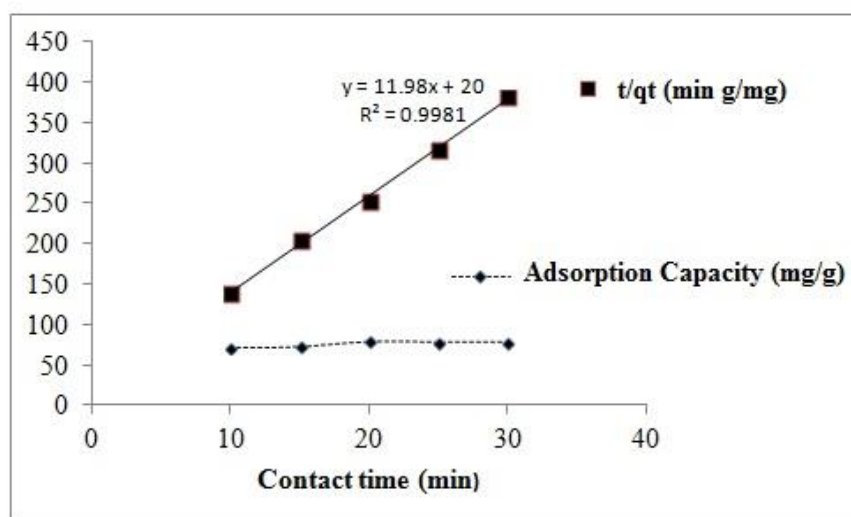
A quantitative depiction of the extent of relationship among the concentration of the adsorbed, adsorbate and their mutual interactive behavior [19] may be done by studying the corresponding adsorption isotherm. These isotherms display graphically the relative variation of the concentration of  $\text{Zn}^{2+}$  in the solid-phase and the solution-phase.

An adsorption on the surface (of adsorbent), having definite sites of equal energy, would be monolayered if the Langmuir's isotherm model fits well with the experimental data. Such befitting nature would indicate that the adsorbed molecules are mutually non-interactive and the degree of the surface coverage does not influence the chemisorptions of  $\text{Zn}^{2+}$ . The commonly used linearized form of the Langmuir model [20] may be expressed as:

$\frac{1}{q_e} = \frac{1}{q_{\max}} + \left( \frac{1}{q_{\max} K_L} \right) \frac{1}{C_e}$ , where  $q_e$  ( $\text{mg g}^{-1}$ ),  $q_{\max}$  ( $\text{mg g}^{-1}$ ),  $C_e$  ( $\text{mol dm}^{-3}$ ) would respectively correspond to the amount of  $\text{Zn}^{2+}$  (at equilibrium) adsorbed by the adsorbent, the concentration of  $\text{Zn}^{2+}$  (at equilibrium with the adsorbent) in the solution, the monolayer adsorption capacity of the adsorbent, while,  $K_L$ , the Langmuir adsorption constant ( $\text{dm}^3 \text{mg}^{-1}$ ) relates the free energy of adsorption (Fig. 7).

The separation factor,  $R_L$ , which is indicative of the adsorbent's affinity for the target ( $\text{Zn}^{2+}$ ), could be determined with the following equation:  $R_L = \frac{1}{1 + K_L C_0}$ , with  $C_0$  = initial concentration of  $\text{Zn}^{2+}$ . The value of  $R_L$  reflects irreversibility

( $R_L = 0$ ), favorability ( $0 < R_L < 1$ ), linearity ( $R_L = 1$ ) or unfavorability ( $R_L > 1$ ) of the Langmuir's isothermal adsorption. Here, the calculated value of  $R_L$  was calculated to be 0.968, which is closer to unity and thus reflects the linearity and favorability of the adsorption process. A physisorption, with infinite surface coverage, would be well represented by Freundlich's isotherm model [20, 21] which predicts a heterogeneous surface with exponential distribution of energies as well as active sites. The following equation:  $\log q_e = \log K_F + \frac{1}{n} \log C_e$ , would represent Freundlich's adsorption isotherm. Here,  $K_F$  ( $\text{dm}^3 \text{g}^{-1}$ ) and  $n$  are constants representing Freundlich's adsorption capacity and adsorption intensity, respectively. From the intercept, the value of  $K_F$  was calculated to be  $10.32 \text{ dm}^3 \text{g}^{-1}$  (Fig. 8), while the slope (which equals  $1/n$ ) was less than 1 which indicated the degree of non-linearity between the residual concentration of  $\text{Zn}^{2+}$  (in the solution) and the amount of adsorbed (in the solid phase).



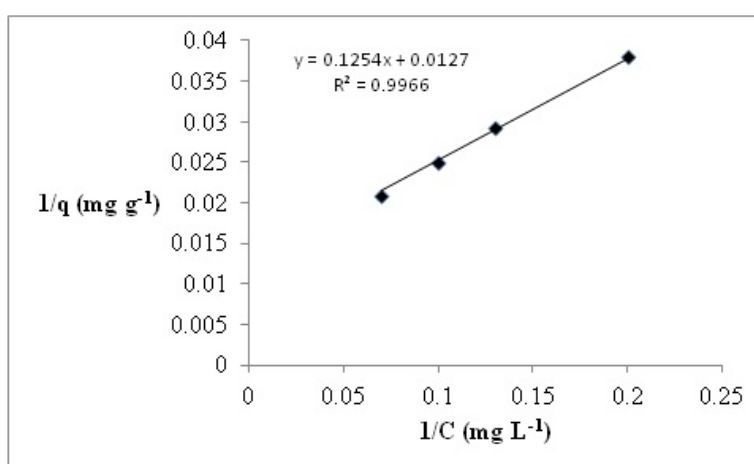
**Figure 6:** Effect of time on (adsorption capacity) and pseudo-second-order kinetics.

### 3.6. Error analysis

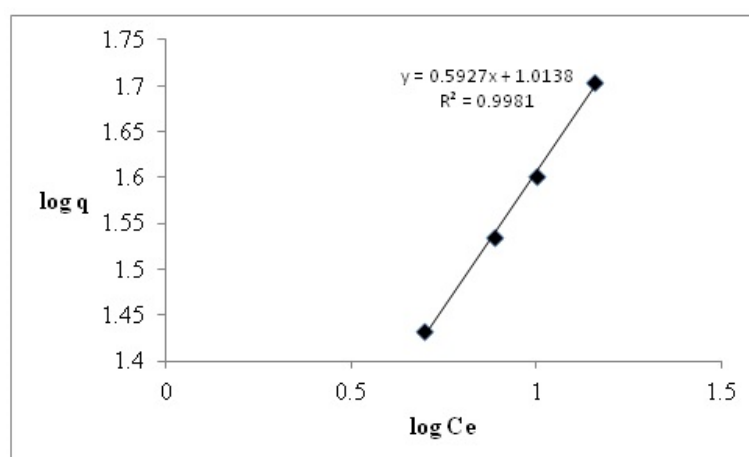
The Chi-square test [15] involves the following equation:  $(Chi - square) \chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}}$ , where  $q_{e,m}$  (mg/g) and  $q_e$  (mg/g) were the equilibrium capacities calculated from the model and obtained in the experiment, respectively. The smaller value of  $\chi^2$  would indicate the closer or the more befitting model. On considering  $R^2$  values of Langmuir's and Freundlich's isotherm models, both apparently seem equally befitting. However, the calculated values of  $\chi^2$  were found to be 0.0007 and 450.2884 for Langmuir's and Freundlich's isotherm models, respectively, whereby suggesting the closeness of the mechanism of adsorption to the former model.

### 3.7. Re-usability

The chelate complex gets disrupted with the eluent, HCl (0.002 M), whereby releasing (and carrying along) the doubly-positively charged ( $Zn^{2+}$ ) ion and thus the adsorbent gets regenerated.



**Figure 7:** Relationship between the concentration of  $Zn^{2+}$  in the solution and the adsorbent through Langmuir isotherm model.



**Figure 8:** Freundlich isotherm model depicting the relationship between the concentration of  $Zn^{2+}$  in the solution and the adsorbent.

## 4. Conclusion

The abundantly available soil has exhibited as a potential support for the development of an adsorbent for heavy metals. The results of the kinetic and isothermal analyses reflect the fast and enhanced adsorption capability of the



adsorbent. The successful modification and the promising nature of the adsorbent were reflected in the SEM-EDX and FTIR analysis. This method promises to conserve the environment by applying the naturally available raw materials in wastewater treatment.

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