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INORGANIC PARTICULATES IN REMOVAL OF TOXIC HEAVY METAL IONS

IV. EFFICIENT REMOVAL OF ZINC IONS FROM AQUEOUS SOLUTION BY HYDROUS ZIRCONIUM OXIDE

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Adsorption behavior of zinc ions on hydrous zirconium oxide (HZO) in aqueous solution has been studied as a function of concentration (10^{-2}–10^{-8}M), temperature (303–333 K) and pH 3–8 of adsorptive solution applying radiotracer technique. The kinetics of adsorption follows first order rate law and agrees well with the classical Freundlich isotherm in the entire range of adsorptive concentration. The removal was found to be increasing with pH of the adsorptive solution while it was suppressed in the presence of acid concentrations. The overall process is found to be endothermic and irreversible in nature.

While certain heavy metal ions (e.g., Hg, Pb, Cd) are toxic, zinc is an essential trace element for enzyme activators in humans, but also becomes toxic at levels of 100–500 mg/day. Significant quantity of zinc enter our water ways from metal production finishing units, industries using zinc and its compounds, preparation of paints and fungicides.[1–4] To keep our aquatic life and their habitat from serious threat of its toxic and non-biodegradable nature, the most effective remedial action is almost a complete removal (up to the permissible levels) of these metallic species from effluents and water bodies.

Hydrous oxides of polyvalent metals have a great potential to be used as adsorbent for the removal of toxic metal ions from aqueous solution and pH of the bulk aqueous soution is an important variable which controls the adsorption of cation by oxide–water interface. A rapid increase in the uptake of zinc ions on amorphous iron oxide from almost zero upto 100%, was noticed by MUSIC and RISTIC[5] when pH was changed from 5.5 to 8.0. A similar maximum adsorption of zinc on hydrous lead dioxide surface was achieved above pH 6.0.[6] The adsorption of zinc on α-alumina and manganese(IV) oxide was found to be increasing with temperature.[7,8] Whereas, a strong suppression of

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zinc adsorption was observed on hydrous iron oxide in presence of Na–EDTA.[9] Adsorption of zinc on a number of oxides under various related parameters was subject of several studies.[10–14]

Hydrous zirconium oxide (PZC 6.7) is one of the most promising adsorbent for anions as well as cations. Recently, we have studied the adsorption of toxic mercury ion on hydrous zirconium oxide using radiotracer technique and results were very promising.[15] In continuation, our present paper deals with adsorption of zinc on hydrous zirconium oxide as a function of adsorptive concentration, temperature and pH of adsorptive solutions. In addition to this, adsorption in the presence of some monovalent and divalent cations as well as different acid concentration have also been seen.

Experimental

Synthesis of hydrous zirconium oxide: Hydrous zirconium oxide was prepared by slow addition of 1M sodium hydroxide solution to $ZrOCl_2 \cdot 8H_2O$ solution heated to about 343 K under constant stirring as reported by MAHAL et al.[16] The precipitate was digested at the same temperature for ca. 2 hours and then allowed to cool. The precipitate was kept in contact with the mother liquor for ca. 48 hours. The precipitate was then filtered, washed several times with distilled water till the filterate was free of alkali ion and then the solid was dried at ca. 323 K. The solid product obtained was broken up in water, filtered and dried at room temperature. Adsorption experiments were carried out using the synthesized material of 120 mesh size.

Infrared and X-ray diffraction analysis: Infrared spectra of the synthesized hydrous zirconium oxide was obtained in the range of 400–4000 cm^{-1} using KBr disc method employing a Jasco FT/IR-5300 spectrophotometer. A broad absorption peak was seen in the range 3000–3500 with a maximum at 3433 cm^{-1}, due to the sum of contributions from interstitial water and hydroxyl groups. At 1626 cm^{-1} a band was also seen which is due to the bending vibrations of water molecule. Some other peaks observed between 800 and 1050 cm^{-1} indicate the presence of Zr–O–H groups in the hydrous zirconium oxide.[17]

The synthesized compound was also characterized by X-ray diffraction using a Philips X-ray diffractometer (PW 1710) giving Cu K_α radiation. X-ray diffraction analysis showed that the synthesized compound was amorphous in nature.[16]

Sorption measurements: Zinc chloride solutions of desired concentrations were prepared from a stock solution of 0.1M $ZnCl_2$ by successive dilution. Radiotracer (^{65}Zn 243.6 d) as zinc chloride in dilute HCl solution was obtained from the Board of Radiation and Isotope Technology (BRIT) Bombay, India was used for labelling adsorbate solutions. The adsorption of zinc(II) ions was investigated by taking 0.1 g of hydrous zirconium oxide in 10.0 ml of zinc chloride solution of known concentration and pH labelled with ^{65}Zn. Beta-activity of the aliquots withdrawn before and after addition of hydrous zirconium oxide at regular intervals of time was measured with the help of an end window G.M. counter (ECIL-1600). The experimental procedure for the estimation of amounts adsorbed and percentage adsorption were identical to those of our earlier report.[18]

Resuts and discussion

Effect of concentration

The concentration dependence study (10^{-2}–10^{-8}M) on the adsorption of zinc(II) on hydrous zirconium oxide as a function of contact time (see Fig. 1) reveals a rapid initial rise in adsorption and thereafter gradual slowing down and finally reaching to an apparent equilibrium. The time taken for reaching equilibrium was found to be ca. 30 minutes at all concentrations of the adsorptive solution. The results show that the amount adsorbed at equilibrium increased from $0.951 \cdot 10^{-9}$ to $0.652 \cdot 10^{-3}$ mol · g^{-1} with the increase in adsorptive concentration from 10^{-8} to 10^{-2}M. This would mean that the relative change in the uptake, i.e., percent adsorption, increases from 65.2 to 95.1% with the dilution increasing from 10^{-2}M to 10^{-8}M at pH 6.88. This increase in the uptake is due to a relatively smaller number of adsorptive species available for an equal number of surface sites of hydrous zirconium oxide.

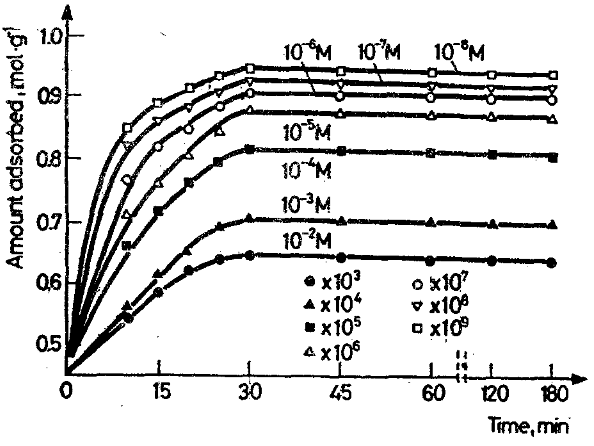


Fig. 1. Time variation of adsorption of Zn(II) ions on hydrous zirconium oxide at various concentrations of $ZnCl_2$ solution. Temperature = 303 K; pH 6.88

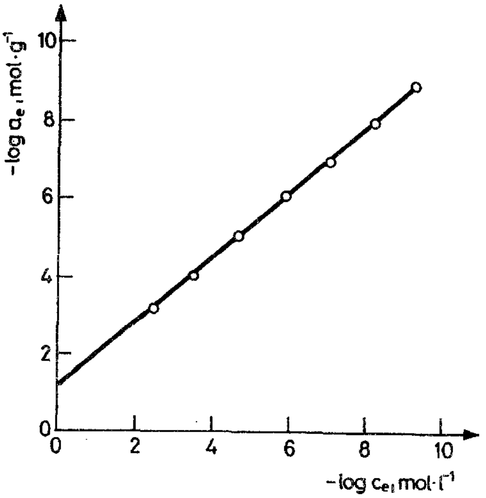


Fig. 2. Freundlich adsorption isotherm for Zn(II) ions on hydrous zirconium oxide at 303 K

Adsorption data were further analyzed using the Freundlich adsorption isotherm (Fig. 2) in its logarithmic form:

$$\log a_e = \log K + \frac{1}{n} \log C_e \tag{1}$$

where a_e is the amount adsorbed at equilibrium, C_e is the equilibrium bulk concentration, K and $1/n$ are Freundlich constants. These constants were estimated from the intercept and slope of the straight line. In the present case, the isotherm with $1/n$ equal to 0.83 ($0 < (1/n) < 1$) is necessarily due to the heterogeneous nature of the surface structure with exponential distribution of surface sites.[19] The observed Freundlich constant K of $6.30 \cdot 10^{-2}$ mol · g^{-1} further confirms a significant affinity to the hydrous zirconium oxide towards zinc(II) ions. The applicability of the Freundlich isotherm has also been reported previously for the adsorption of zinc ions on titanium dioxide and manganese dioxide.[10,14]

Effect of temperature

The uptake of zinc(II) ions on hydrous zirconium oxide has been studied as a function of temperature (303–333 K) with $1.0 \cdot 10^{-6}$M zinc(II) solution at pH 6.88. The results (Table 1) reveal that the amount of zinc adsorbed on hydrous zirconium oxide increased slightly from $0.913 \cdot 10^{-7}$ to $0.939 \cdot 10^{-7}$ mol · g^{-1} on increasing the

Table 1
Temperature variation study on amount of Zn(II) ions adsorbed and desorbed on hydrous zirconium oxide at equilibrium.
Initial concentration of adsorptive = $1.0 \cdot 10^{-6}$M; pH 6.88

Temperature, K	Amount of Zn(II) ± 3σ adsorbed		Desorption in equilibrium bulk concentration, %
	$\times 10^7$ mol · g^{-1}	Adsorption, %	
303	0.913 ± 0.003	91.3	4.7
313	0.921 ± 0.007	92.1	4.9
323	0.932 ± 0.008	93.2	5.0
333	0.939 ± 0.005	93.9	.5.3

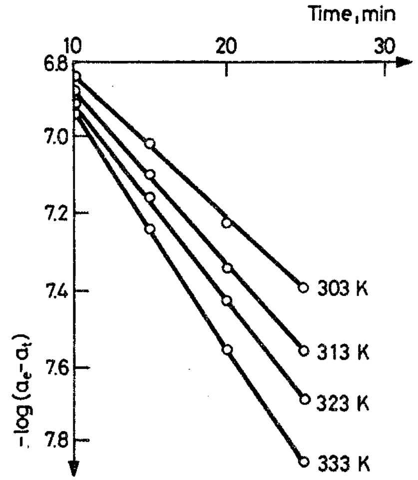


Fig. 3. Plot of log $(a_e - a_t)$ vs. time for the adsorption of Zn(II) on hydrous zirconium oxide at various temperatures. Initial concentration of Zn(II) solution = $1.0 \cdot 10^{-6}$M; pH 6.88

temperature from 303 to 333 K. This increase in the amount adsorbed at equilibrium with temperature is considered to be due to the creation of some new active sites on the adsorbent surface or due to the acceleration of some originally slow adsorption steps. A similar increase in the uptake of zinc on α-alumina and manganese oxide with a rise in temperature has been reported.[7,8]

The order of reaction for the adsorption of zinc ions by hydrous zirconium oxide has been worked out and the results follow Lagergren equation in the form

$$\log (a_e - a_t) = \log a_e - \frac{k_1}{2.303} \cdot t \tag{2}$$

Table 2

Kinetic parameters ± 3σ for adsorption of Zn(II) ions on hydrous zirconium oxide as a function of temperature. Initial concentration of Zn(II) solution = $1.0 \cdot 10^{-6}$M; pH 6.88

Temperature, K	Rate constant, $\times 10^2$min^{-1}	Activation energy, kJ · mol^{-1}	Enthalpy change, kJ · mol^{-1}
303	8.75 ± 0.03	13.07 ± 0.03	10.21 ± 0.06
313	10.59 ± 0.05		
323	11.98 ± 0.02		
333	13.98 ± 0.07		

where a_e is the amount of zinc adsorbed at equilibrium, a_t is the amount of zinc adsorbed at time t, k_1 is adsorption rate constant at different temperatures. The plot of log $(a_e - a_t)$ vs. time gives straight line (Fig. 3) showing that the process follows a first order rate law. The value of rate constants so deduced are returned in Table 2.

The equilibrium values of adsorption at different temperatures have been utilized to evaluate the change in standard enthalpy (ΔH^0) using following equations

$$\log K_D = -\frac{\Delta H^0}{2.303R} \cdot \frac{1}{T} + \text{constant} \tag{3}$$

where

$$K_d = \frac{\text{Radioactivity adsorbed/g of adsorbent}}{\text{Radioactivity of equilibrated solution/ml}} = \frac{R_0 - R_e}{R_e} \cdot \frac{V}{m} \quad \text{ml} \cdot \text{g}^{-1} \tag{4}$$

Here the terms R_0 and R_e represent the initial and equilibrium radioactivity of the bulk, V is the volume, ml, of adsorbate and m is the amount of adsorbent. The value of ΔH^0, estimated from the slope of straight line plot [log K_d vs. $(1/T)$], was found to be positive (10.2 kJ · mol^{-1}) indicating the process to be endothermic and "ion exchange" in nature.[20]

Furthermore, the activation energy for the adsorption of zinc(II) ions has also been estimated through Arrhenius plot (viz. log k_1 vs. $1/T$) using the values of rate constants at different temperatures. The value of activation energy, found to be 13.07 kJ · mol^{-1} for the present system, indicates that the forces of attraction operating during adsorption of zinc ions on hydrous zirconium oxide are strong enough and the uptake process can occur even under ordinary conditions.

Effect of pH

The study of pH dependence on the adsorption of Zn(II) ions on hydrous zirconium oxide was made from bulk concentration of $1.0 \cdot 10^{-6}$M at different pH values in the range of 3.1–7.9. The experimental results were analyzed by plotting the amount adsorbed at equilibrium as a function of pH (Fig. 4) and show that the amount of Zn(II) ions adsorbed at equilibrium increases from $0.236 \cdot 10^{-7}$ to $0.946 \cdot 10^{-7}$ mol $\cdot$ g^{-1} wih the increase in pH from 3.1 to 7.9. It is also apparent that the uptake of Zn(II) ions increases gradually upto pH 6.08, after that a sharp increase in the uptake was found. A similar behavior of increased ion adsorption on increasing pH has been reported in the literature.[5,6,9,10,14,21]

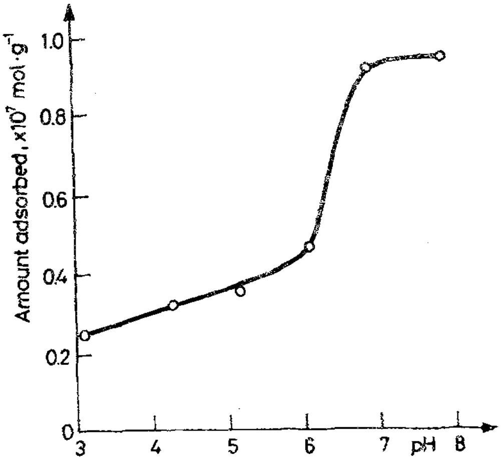


Fig. 4. Effect of pH on adsorption of Zn(II) ions on hydrous zirconium oxide at equilibrium point. Initial concentration of Zn(II) solution = $1.0 \cdot 10^{-6}$M; temperature = 303 K

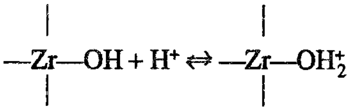
Generally, the strong pH dependence of the adsorption of divalent cations has been interpreted in terms of several mechanism: preferential adsorption of hydroxo complexes such as MOH^+, formation of surface $M(OH)_x$ compounds or the exchange of M^{2+} with surface protons at the oxide/H_2O interface.

$$ZrOH + Zn^{2+} \rightleftharpoons ZrO^- \cdot Zn^{2+} + H^+$$

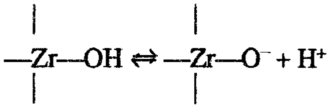
$$ZrOH + Zn^{2+} + H_2O \rightleftharpoons ZrO^- \cdot Zn(OH)^+ + 2H^+$$

$$ZrOH + Zn(OH)_2(aq) \rightleftharpoons ZrOH \cdot Zn(OH)_2$$

The hydrated zirconium oxide–water interface can acquire charge by protonation or deprotonation of neutral sites (surface hydroxyl groups) according to following mechanism:



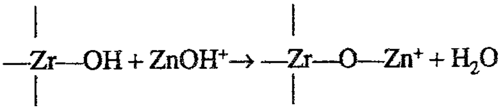
$$-\mathrm{Zr}-\mathrm{OH} + \mathrm{H}^+ \rightleftarrows -\mathrm{Zr}-\mathrm{OH}_2^+$$



$$-\mathrm{Zr}-\mathrm{OH} \rightleftarrows -\mathrm{Zr}-\mathrm{O}^- + \mathrm{H}^+$$

Thus, it apparent from the above reactions, that in highly acidic medium the hydrous zirconium oxide is strongly positive and shows a relatively weak affinity for Zn(II) ions. As the pH value of the bulk solution increases the positive character of the surface decreases due to dissociation of hydronium ion (increase in OH^- ions) and shows a greater tendency towards the surface uptake of cations; and as a consequence of this the adsorption of Zn(II) ions increases. Adsorption on hydrous oxide depends not only on the ionization of the surface hydroxyl group but also on the relative affinities of $[Zr\text{–}O^-]$ for hydronium ion and Zn(II) ions, that is, on the readiness with which zinc associates with the oxygen in the matrix. The inflexion point of the pH–curve (Fig. 4) corresponds to a point of zero charge being at 6.7.[22] It is the pH beyond which the hydrous zirconium oxide has negative surface charge and behaves as cation exchanger.

Zinc does not hydrolyze at $pH \leq 4$ and occurs as cationic species $[Zn^{2+}]$. At $pH \geq 5$, Zn^{2+} gets hydrolyzed to some extent in acidic media (upto pH 7) resulting in the formation of soluble $[Zn(OH)^+]$ species. However, it should be noted that on further increase of pH (≥ 7.5) the predominant species of zinc in solution are known to be hydroxo complexes such as $[Zn(OH)^+]$ and $[Zn(OH)_2^0]$.[23,24] Nucleation of $[Zn(OH)_2]$ clusters on oxide surface is another possibility for the uptake in alkaline pH range.[25] Hence, the adsorption of hydrolyzed species should also be taken into consideration. The increase in adsorption of Zn(II) ions on hydrous zirconium oxide with increasing pH is thus explicable by the mechanism of hydrolytic adsorption as:



$$-\mathrm{Zr}-\mathrm{OH} + \mathrm{ZnOH}^+ \rightarrow -\mathrm{Zr}-\mathrm{O}-\mathrm{Zn}^+ + \mathrm{H_2O}$$

Thus, the surface charge and the extent of hydrolysis are expected to increase with increasing pH, resulting into more adsorption of Zn(II) ions on hydrous zirconium oxide.

Desorption study

Hydrous zirconium oxide with pre-adsorbed zinc ions was washed with double distilled water to ensure the removal of adhering species and subsequently the adsorbent was dried in an electric oven at 383 K. The desorption of pre-adsorbed zinc ions on hydrous zircnium oxide surface was studied in zinc chloride ($1.0 \cdot 10^{-6}$M) solution at different temperatures. The values of percentage desorption at different temperatures are returned in Table 1. It is apparent that the desorption process is almost independent of temperature. Thus, a very low value of desorption, unaffected by increase of temperature, shows that the process of adsorption in zinc ions by hydrous zirconium oxide is irreversible in nature. It also indicates that a major portion of zinc ions was, probably, bound to hydrous zirconium oxide through strong interaction and are converted to a final stable adsorption phase.

Effect of other ions and acid concentrations

The effect of the presence of some monovalent and divalent cations ($6.0 \cdot 10^{-5}$M) was investigated on the adsorption of zinc ions ($1.0 \cdot 10^{-5}$M) on hydrous zirconium oxide. Percentage adsorption of zinc in the presence of Na^+, K^+, Ba^{2+} and Sr^{2+} (all as chlorides) was found to 84.9%, 83.5%, 80.4% and 81.6%, respectively, while in the absence of these cations the adsorption of zinc ions from solution of concentration $1.0 \cdot 10^{-5}$M was 88.3%. This variation in adsorption capacity of hydrous zirconium oxide may be due to competitive adsorption between added cations and zinc ions.[26]

The addition of three fold concentration of some sodium salts having different co-anions, e.g., sodium sulphate, sodium acetate and sodium phosphate also resulted in reduced adsorption of zinc on hydrous zirconium oxide and this reduction was slightly more with respect to sodium chloride. Thus, it is found that the percentage adsorption decreases from 88.3% to 80.3%, 76.9% and 68.4% for sulphate, acetate and phosphate ions, respectively. This additional reduction is obviously due to co-anions (viz. sulphate, acetate and phosphate) present in the bulk alongwith Na^+ ions and adsorptive ions (Zn^{2+}) which may be preventing the adsorption of Zn^{2+} to some extent.

The relative adsorption of zinc ions on hydrous zirconium oxide in the presence of strong metal complexer EDTA has also been studied. For the concentration ratio $[Na\text{–}EDTA]/[Zn^{2+}] = 3$, the effect on zinc adsorption was quite pronounced as the adsorption of zinc decreased to 47.5% while it was 88.3% in ligand free solution. Metal organic complexes are often stable and anionic over a wide range of pH. [Na–EDTA] converts the zinc ions into anionic complexes like $[Zn\text{–}H\text{–}EDTA^-]$ and $[Zn\text{–}EDTA^{2-}]$ which gives reduced adsorption. Also, [Na–EDTA] may complex zinc ions to such an extent that the "free" zinc concentration decreases causing a decrease in adsorption.

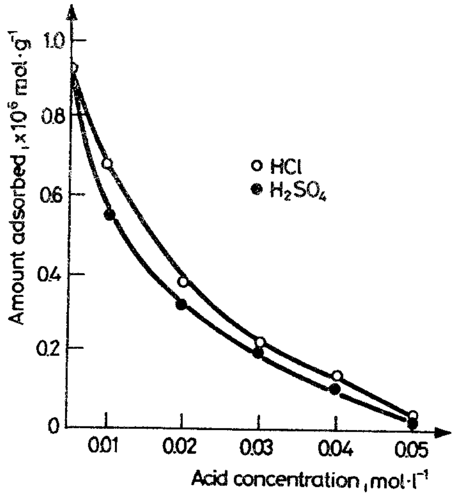


Fig. 5. Effect of acid concentration on adsorption of Zn(II) ions on hydrous zirconium oxide. Temperature = 303 K; initial concentration of Zn(II) ions = $1.0 \cdot 10^{-5}$M

However, non-adsorption of [Zn–EDTA] complex on HZO is not the only factor responsible for the suppression in zinc adsorption as EDTA has a strong affinity towards oxide surfaces.[27]

Furthermore, the adsorption of zinc was investigated as a function of hydrochloric acid and sulphuric acid concentrations in the range of 0.005–0.05M. The results indicate that the adsorption of zinc was slightly decreased at an acid concentration of 0.005M while at 0.05M acid concentration it becomes almost insignificant (Fig. 5). This is considered due to a competition between the excess H^+ in the adsorptive solution and positively charged hydrolyzed zinc species.

Conclusions

The uptake of Zn(II) ions on hydrous zirconium oxide is favoured at higher concentrations and higher temperatures of the bulk solution. The kinetics of adsorption process follows first order rate law and obeys the classical Freundlich isotherm, and the process involved appears to be "ion exchange" in nature. In presence of some ions, EDTA and acid concentrations, a suppression in the zinc uptake by HZO is observed.

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