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Investigations on sorption performance of some radionuclides, heavy metals and lanthanides using mesoporous adsorbent material

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Abstract Synthesis and characterization of potassium zinc hexacyanoferrate (KZnFC) as nano ion exchanger material are performed. Sorption characterization investigations on the removal of some radionuclides (^{134}Cs, ^{60}Co), heavy metal (Pb^{2+}) and lanthanides (Ce^{3+} and Gd^{3+}) from aqueous and nitric acid solutions using mesoporous KZnFC ion exchange have been done. Selective removal of ^{134}Cs rather than ^{60}Co and Ce^{3+} (lanthanides) is achieved in aqueous solution and nitric acid solution, respectively. The maximum sorption capacity of ^{134}Cs, ^{60}Co, Pb^{2+}, Ce^{3+} and Gd^{3+} is 170, 10.5, 3.88, 0.72 and 0.55 mg/g, respectively, onto nano-material of KZnFC.

Keywords Equilibrium · Kinetic · Ion exchange · Removal · Capacity and sorption

Introduction

Cesium and Cobalt are the most abundant radionuclides in nuclear fission products that are routinely or accidentally released. They have relatively long half-life and are considered as hazardous elements for the environment. Various methods such as evaporation, ion exchange and chemical precipitation are applied for the treatment of aqueous waste solutions containing these ions [1–4]. ^{137}Cs and ^{135}Cs are the longest half-life of cesium isotopes with 30.16 years and 2.3 million years, respectively. ^{137}Cs is produced from nuclear weapons testing and in thermal reactors. ^{134}Cs has a 2.065 years half-life, and it is produced as an activation product in nuclear reactors. It has been found that cesium is tightly bound by the clay minerals of the soil that root uptake is slight. Therefore, foliar absorption is the main portal of entry of ^{137}Cs to the food chains. The uptake of Cs from the soil has been shown to be inversely proportional to the K content of soils in which there is a potassium deficiency [5].

In aqueous solution, cesium is hydrated and the exchange of water between the hydrated ion and the solvent is extremely rapid. Although there is evidence for the formation of weak complexes of alkali metal ion in aqueous solution yet the isolation of solid complexes from this medium is very difficult. For this reason, it is much preferable to work in organic solvents [6].

Cobalt-60 ($T_{1/2} = 5.272$ years) is formed in a nuclear fission process during the operation of a nuclear power reactor by activation of ^{59}Co present as an impurity in the metal for which the structural parts of the fuel assemblies are made. The decay energies of ^{60}Co are $E_{\beta} = 0.314$ MeV, and $E_{\gamma} = 1.173$ and 1.332 MeV [7]. Because of higher energies of γ-radiation and long half-life, large quantities of cobalt-60 are used as γ-ray sources for various applications in research, industry and medicine [8]. In the simple cobalt compounds, the divalent forms are more stable. Cobaltous ion, Co^{2+} is basic and generally exists in a hydrolyzed form. Cobalt is of biological significance because it forms organic complexes under favorable conditions. The release of cobalt into the environment includes the deposition and retention in the sediment which due to a partial fixed by the humic materials present and a part deposited as a coagulant. [9].

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Lead is the most abundant heavy metal in the earths. The naturally occurring isotopes of Pb (206, 207 and 208) is arising as the stable end products of the decay of natural radioactive series [10, 11]. Once Pb enters the environment, its chemistry is dominated by the Pb^{2+}. Lead has also oxidation state of Pb^{4+}, but it is no stable region exists for Pb^{4+} except at very high oxidation potentials and basic conditions [12]. Lead released to natural environment by many industries that is ranked as the number one environmental health threat, by the U.S. Agency for Toxic Substances [13]. Lead is now recognized as a heavy-metal poison; it acts by complexing with oxo-groups in enzymes and affects virtually all steps in the process of haem synthesis and are colic, anaemia, headaches, and convulsions, chronic nephritis of the kidneys, brain damage and central nervous-system disorders [11].

Gadolinium is used in fabrication of fuel and used as a control rod in the core of nuclear reactor as well as in ceramic industries. It has been used as neutron poison in heavy water reactors. A concentration of 15 and 2 µg/mL of Gd have been injected during emergency shutdown and at start-up of the rector in heavy water moderators [14, 15]. Moreover, radiolanthanides elements (such as ^{144}Ce, $^{152,\ 154,\ 155}$Eu, ^{153}Gd…etc.) are a fission products and presented in liquid radioactive waste. In view of environmental issue the leaked of radioisotopes and industrial toxic elements are caused a significant risks to human and all beings system. Thus it is considered as removal of towards ^{134}Cs, ^{60}Co, Pb^{2+}, Ce^{3+}, La^{3+} and Gd^{3+} from radioactive liquid waste and/or industrial wastewater are extremely challenge not only for their economic reasons, but also for reducing their contamination to the water environment.

Several inorganic adsorbent such as sodium titanates, zeolites, silicotitanates and hexacyanoferrates [16, 17] were used in nuclear sites for the treatment of nuclear wastes. Ion exchange materials are characterized by their ability with regards to radiation and temperature, thus they can be used in treating highly radioactive waste solutions [18]. Several applications of ferrocyanide exchangers to remove radioactive cesium have been reported [19, 20]. Removal of ^{137}Cs and ^{131}I using ion-exchanger of ferrocyanide form water and milk, respectively, as emergency countermeasures were studied by Watari et al. [21]. KCoFC, KNiFC, and KCuFC can be applied to separate trace amounts of the Cs ion from the surrogate soil decontamination solution [22]. Taj et al. [17], used potassium iron (III) hexacyanoferrate(II) for the strontium(II) removal from of nitric and hydrochloric acids solutions. Removal of cesium by composite material of poly methyl methacrylate-KFeCN has been investigated [18]. Decontamination of toxic metals from wastewater that associated with industry activities is necessary from the stand point of environmental pollution control [16]. Various processes for wastewater treatment such as ion exchange, precipitation, redox, and solidification are used for metal removal. The adsorption isotherms of Pb(II) ions from wastewater by maize husk has been studied. Harmful level of Pb ions in human organs were associated with mental retardation, encephalopathy, and seizures [23]. In our previous investigation organic polymer [24], composite material [2], activated carbon [25], natural material [26] and inorganic adsorbent as ion exchanger [27] have been successfully applied for recovery of different radioisotopes as well as lanthanides elements. In this context, we aim to prepare potassium zinc hexacyanoferrat (KZnFC) of specific characteristic for effective treatment of some fission products (^{134}Cs, ^{60}Co, $^{144}Ce^{3+}$ and $^{153}Gd^{3+}$) and toxic metal ($^{60}Co^{2+}$ and Pb^{2+}) from radioactive waste and/or wastewater as nano-inorganic sorbent material. The comparative on selectivity and sorption characteristic of the prepared material towards radioactive liquid waste and/or contaminated wastewater are evaluated for emergency case of environmental contamination.

Experimental

Chemicals and reagents

All the reagents used in this work were of AR grade chemicals and were used without further purification. Distilled water was used for washing all glassware and preparing solutions. The solid phase used is potassium zinc hexacyanoferrate ion exchange. Potassium zinc hexacyanoferrat (KZnFC) was prepared using 0.5 M aqueous $K_4Fe(CN)_6$, the solution was added with stirring to 0.25 M aqueous $Zn(NO_3)_2$ with 1:1 volume ratio. The potassium zinc-hexacyanoferrat precipitated at 100 °C. The precipitate was removed, washed, dried to constant weight at 100 °C, subsequently pulverized and fractionated by sieving. The finest grains fraction of particle size ~ 0.1–0.35 mm was used for the investigations carried out through this work.

Sorption experiments

Batch sorption studies of ^{134}Cs, ^{60}Co, Pb^{2+} and Ce^{3+} were performed from different concentration of nitric acid solution. Sorption properties of binary system of ^{134}Cs and ^{60}Co and individual solution of Pb^{2+}, Ce^{3+} and Gd^{3+} from aqueous solution as function of different pH were studied. Kinetic studies were performed at room temperature (298 K) over different shaking time for ^{134}Cs, ^{60}Co, Pb^{2+} from 0.1 M HNO_3 and lanthanides ions under study from aqueous solution at pH 4.5. For isotherm studies, a series of

25 mL polypropylene bottles were employed. Each bottle was filled with 10 mL of Cs^+, Co^{2+}, Pb^{2+} from 0.1 M HNO_3 and Ce^{3+} and Gd^{3+} ions aqueous solution at pH 4.5 of varying concentrations with known amount of ion exchange (100 mg) was added into each bottles and agitated for a sufficiently long time (~ 2 h) required to reach equilibrium. The bottle was kept stirred in a thermostat shaker adjusted at 25 °C ± 1 after that, samples were filtered and the filtrate was analyzed to determine the concentration after sorption process. The concentration of each lanthanides elements (Ce^{3+} and Gd^{3+}) are 10 mg/L in solutions during the experiments. An initial concentration of each ion of Cs^+, Co^{2+}, Pb^{2+} are 100 mg/L. The radioisotopes of ^{134}Cs and ^{60}Co were subjected for radiometric analysis by NaI detector. The atomic absorption spectrophotometry was used to determine the concentration of Pb^{2+}. The concentration of lanthanides elements under study have been measured by UV-spectrophotometric using Arsenazo-III (as complexing agent) at wavelength of 650 nm. The standard and analytical samples solutions were prepared following carefully the instruction of the operational book of the Perkin Elmer 1100 Atomic Absorption Spectrophotometer. In all determination double samples were analyzed for three times to get a reproducibility on them ± 3%. The amount of metal ion retained in the solid phase, q_t, (mg/g) was calculated using:

$$q_t = (C_o - C_t) \times V/m \tag{1}$$

$$Sorption\,(\%) = [(C_o - C_t)/C_o] \times 100 \tag{2}$$

For radioisotopes,

$$(mg/g)\,\mathrm{q_t} = \left(\frac{\mathrm{C_i} - \mathrm{C_f}}{\mathrm{C_i}}\right)\mathrm{C_o}\,\frac{\mathrm{V}}{\mathrm{m}} \tag{3}$$

where C_o and C_t are the initial and equilibrium concentration (mg/L) of metal ion in solution, C_i and C_f are the initial and the final counting rate per unit volume for the radionuclide, respectively; V the volume (L) and m is the weight (g) of KZnFC material.

Analytical methods

The surface area of the sample was determined using Micromeritics Proe Size 9320. Thermal analysis was carried out using thermogravimetric analyzer TGA-50 model Shimadzu at a heating rate of 10 °C/min. The sample X-Ray diffraction patterns were measured using a Shimazdu X-ray diffraction, model XD1180-Japan, 30 mA with Cu-anode. IR samples measurements were carried using a Perkin Elmer 1600 FT-IR spectrometer.

Results and discussion

Characterization of prepared KZn-hexacyanoferrat

The IR spectra of prepared KZnFC was measured in the wavelength region 4000–400 cm^{-1} as shown in Fig. 1. It is showed an intense band in the region 2000–2200 cm^{-1} which is assigned for the active CN^- group characteristic of cyanoferrate compounds. The peaks at 3450–3670 cm^{-1} are characteristic to water molecules. The bands at 1615, 1385 cm^{-1} are assigned to H-OH bending and interstitial water molecules. The 604 and 497 cm^{-1} are characteristic of metals (Zn–K–Fe) oxide bond [28, 29]. The IR spectra measured after the uptake of $^{134}Cs^+$ is showed a decrease in the intensity of this band without any marked shift that revealed the adsorption process occurs onto the prepared material as demonstrated in Fig. 1.

Figure 2 displays the XRD pattern of KZnFC. It was found of cubic structure with a crystal lattice of a 10.5 Å which reflects a nano particles of the prepared KZnFC. The

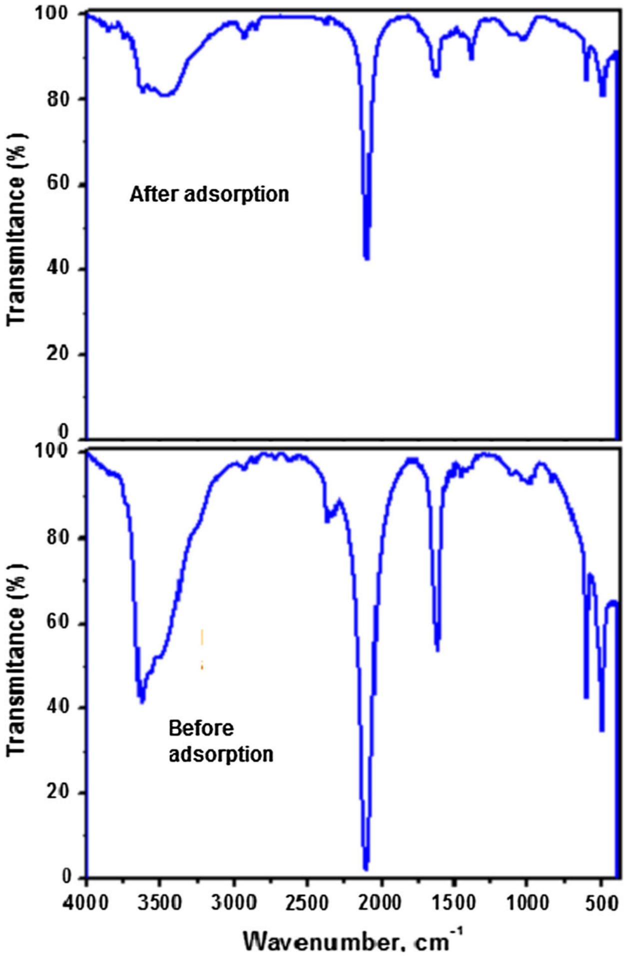


Fig. 1 IR spectra of the prepared KZnFC material

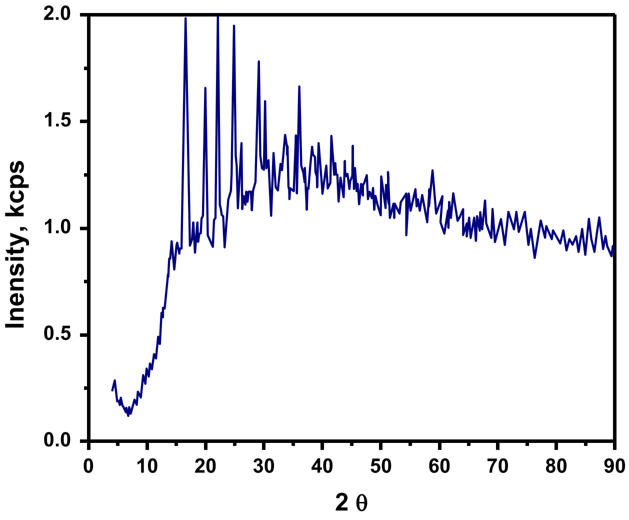


Fig. 2 XRD pattern of KZnFC nano material

obtained peaks are confirmed the successful preparation of nano particles of KZnFC material.

The thermal analysis for the KZnFC powder showed the following; a first weight loss of 6.5% and second weight loss of 4.85% which are attributed to the loss of external and internal of H_2O molecules as demonstrated in Fig. 3. Another weight loss of 5% was observed at the temperature range 470–715 °C which is due to the loss of CN^- groups. The total calculated weight loss of 16.4% is observed over the temperature of 800 °C which revealed that a high thermal stability of the prepared material.

Adsorption desorption of N_2 gas onto KZnFC as shown in Fig. 4. This curves revealed that isotherm type IV according to the IUPAC isotherm, which is typical for mesoporous materials that exhibit capillary condensation and evaporation and that have large pore sizes with narrow size distributions [27]. The Brunauer–Emmett–Teller (BET) surface area, Langmuir surface area, average pore radius and total pore volume of the prepared KZnFC material are 8.20, 13.96 m^2 g^{-1}, 22.45 Å, respectively. These characterization results revealed the successful preparation mesoporous material of KZnFC as nano adsorbent of high thermal stability.

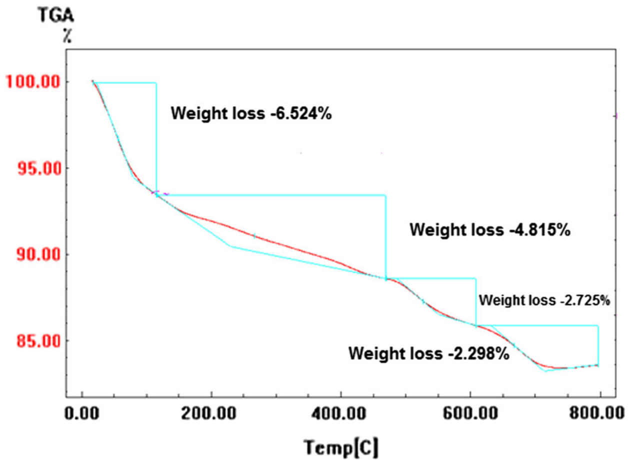


Fig. 3 TGA-DTA of nano material of KZnFC

The SEM pictures of free prepared KZnFC material and loaded KZnFC nano material are shown in Fig. 5. This pictures revealed that the porous surface and promising sorption characteristics of the prepared mesoporous of KZnFC material.

Sorption investigation

The adsorption characteristic of some fission products (^{134}Cs, ^{60}Co, Ce^{3+} and Gd^{3+}) and toxic metal (Co^{2+} and Pb^{2+}) from radioactive waste and/or wastewater using nano inorganic sorbent material were carried out using KZnFC. The adsorption equilibrium was first examined to identify the adsorption behavior and suitable conditions for the adsorption of these ions from nitric solution. In this respect, the effect on contact time, HNO_3 concentration and the initial metal ion concentration on the sorption of these ions onto KZnFC were investigated. The kinetic investigations were performed on KZnFC for ^{134}Cs, ^{60}Co and Pb^{2+} to learn about the mechanism of adsorption by the used adsorbent.

Effect of acidic and pH of solution

To clarify the effect of nitric concentration on sorption of investigated ions onto the prepared KZnFC, the uptake of these ions in different concentrations of HNO_3 has been investigated as seen in Fig. 6. For this purpose 10 mL with different concentrations of HNO_3 solution were prepared containing 100 mg/L Cs, Co, Pb and 10 mg/L of Ce that mixed with 0.1 g of KZnFC at 2 h shaking time. The Figure show that increasing in HNO_3 concentration decrease the uptake percent of cesium, cobalt and Pb uptake in the range (0.1–1.5 M). The decreases in uptake with the increase in hydrogen ion concentration can be attributed to the competition of H^+ ion with metal ions. The increase in the molarity of acid increases the tendency of associated anion (NO_3^-) in the medium to complex the metal ions in the solution and therefore decrease its uptake. It is observed insignificant sorption towards lanthanides (represented by Ce^{3+}) from HNO_3 media. The selectivity order takes the following: Cs > Co > Pb > Ce.

Figure 7 shows the influence of pH of solution on the sorption of lanthanides (Ce^{3+} and Gd^{3+}) and fission products ($^{134}Cs^+$, $^{60}Co^{2+}$). The data reveals that the percentage of sorption gradually increase with increasing pH for all ions except $^{134}Cs^+$ which is no effect on its sorption manner. The low degree of sorption of ions at low values

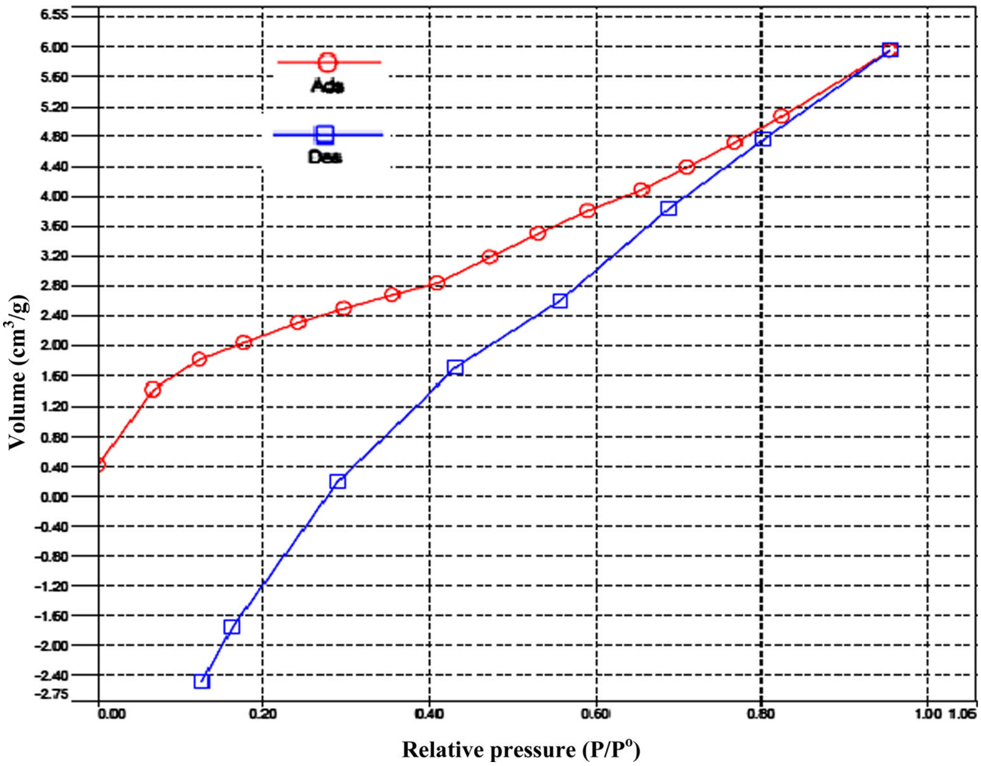


Fig. 4 Adsorption–desorption of N_2 gas onto the prepared KZnFC material

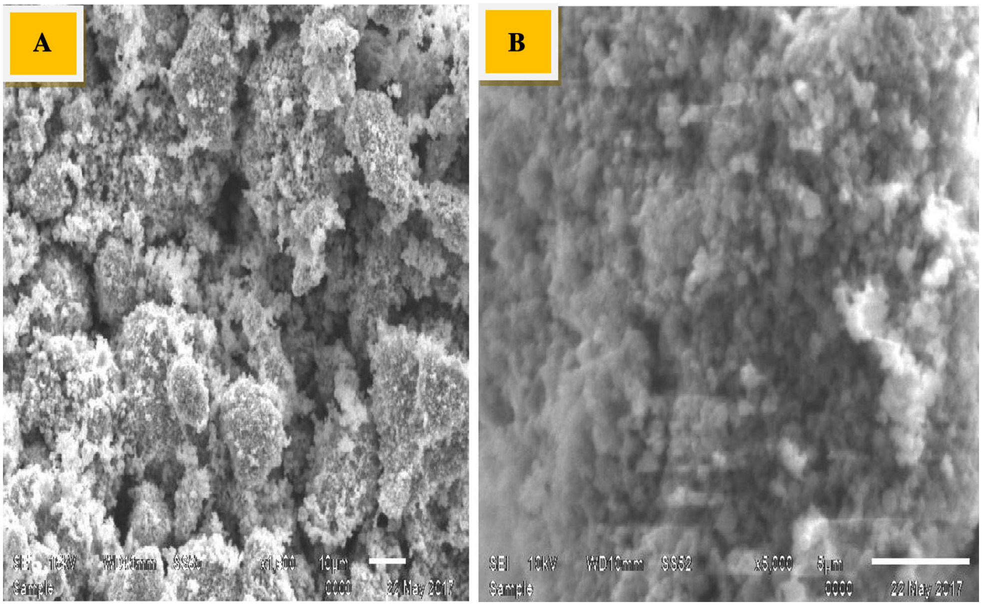


Fig. 5 SEM pictures of (**a**) free KZnFC and (**b**) loaded KZnFC material by $^{134}Cs^+$

pH (2–4), can be attributed by the H^+ ion concentration is high and therefore H^+ ion compete with the cations for surface sites. In addition, decreases of surface positive charge is associated with pH increases, this would result in effect of sorption ions process. Lanthanides are been hydrolysis in aqueous media at pH < 6 and some species of $Ln(OH)^{2+}$, $Ln(OH)_2^+$, $Ln(OH)_3$, $Ln(OH)_4^-$ could be represented in solution. Thus, as pH increases, hydrolysis precipitation most probably would start due to the formation of various hydrocomplexes in aqueous solution. Therefore, pH of 4.5 is selected for next experiments on lanthanides. In case of binary system, the obtained results are demonstrated that a highly selective separation of ^{134}Cs rather than ^{60}Co from the same solution. The speciation of

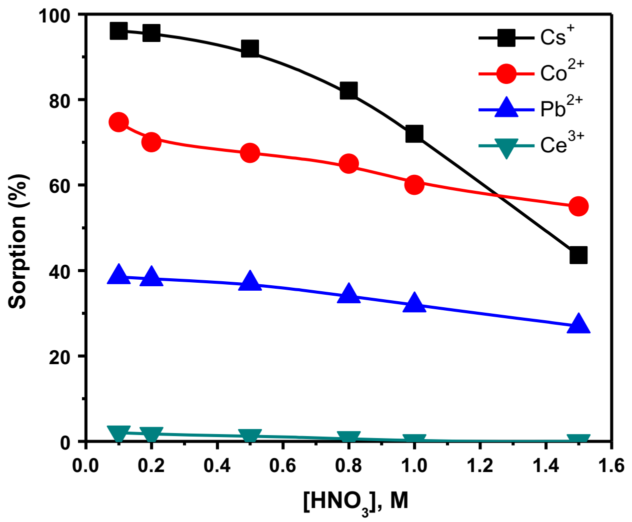


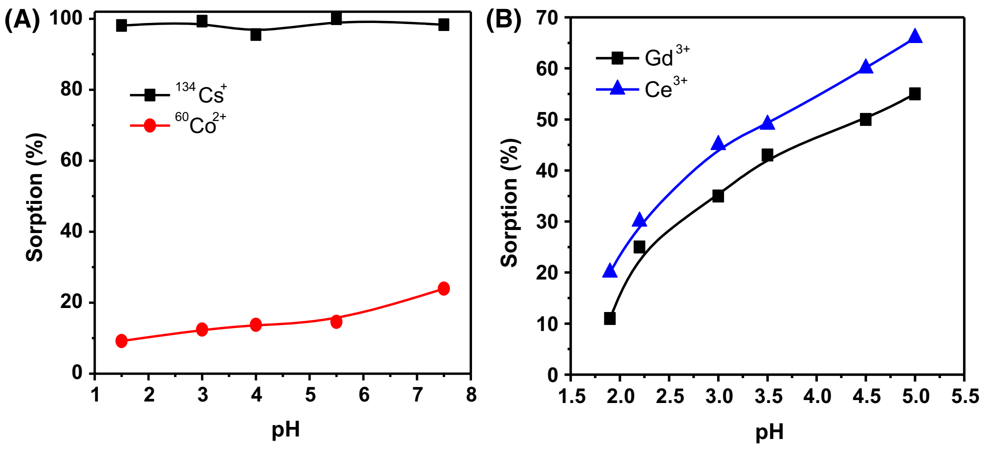
Fig. 6 Effect of HNO_3 concentration on the sorption properties of $^{134}Cs^{+}$, $^{60}Co^{2+}$, Pb^{2+} and Ce^{3+} onto mesoporous KZnFC from HNO_3

Cs and Co at different values of pH in aqueous demonstrated that these ions appeared as Cs^{+} and Co^{2+} at pH < 8. While the $Co(OH)^{+}$, $Co(OH)_2(aq)$, $Co(OH)_2(s)$, and $Co(OH)_3^{-}$ are existed as relevant species undergoes precipitation after pH 8–12. At low pH ranges, ^{60}Co sorption was inhibited due to presence of H^{+} which complete with the Co^{2+} for sorption sites. However, the ^{134}Cs sorption was almost unaffected at pH ranges. It is revealed that a high affinity of mesoporous of KZnFC towards ^{134}Cs from a fission products on aqueous solutions. On the further investigation the fission products from 0.1 M HNO_3 and lanthanides from aqueous at pH 4.5 were carried out.

Effect of contact time

The sorption kinetic of 100 mg/L of $^{134}Cs^{+}$, $^{60}Co^{2+}$ and Pb^{2+} onto KZnFC, from 0.1 M HNO_3 solution as well as 10 mg/L of (Ce^{3+}, Gd^{3+}) from aqueous solution at pH 4.5 was studied. Plots of the amount sorbed of Cs^{+}, Co^{2+} and Pb^{2+} from nitric solution onto 0.1 g of KZnFC, at 298 K, as a function of shaking time are represented in Fig. 8. The figure show a high initial rate of removal within the first 20 min of contact followed by slower subsequent removal rate that gradually approached an equilibrium conditions in about 2 h especially for ^{134}Cs and ^{60}Co. The equilibrium state in case of Ce^{3+} and Gd^{3+} is reached after about 3 h. The high amount of metal sorbed at equilibrium for $^{134}Cs^{+}$, $^{60}Co^{2+}$, Pb^{2+}, Ce^{3+} and Gd^{3+} are 9.73, 8.12, 3.8, 0.6 and 0.5 mg/g, respectively. The rapid uptake of these ions by studied ion exchanger may be due to exchange of the ions with some ion constituents in surface of prepared material and/or adsorption onto the porous of material. It should be noted that the diffusion of ions onto KZnFC is time dependent; therefore pseudo equilibrium is attained when contact time is lengthened. On the basis of these results, 2 h (2 h) of equilibrium time was chosen as the optimum contact time to ensure that equilibrium conditions were achieved. There are a numerous of parameters affecting sorption rates as physical properties of structural adsorbent, metal ion properties, initial ions concentration, pH, temperature, or presence of competing ions [19]. The amount of metal sorbed (q_t) is gradually increase with increasing of time till reach equilibrium state. The equilibrium uptake was reached after 45, 90 and 20 min and about 100 min for sorption of Cs^{+}, Co^{2+}, Pb^{2+} and (Ce^{3+} and Gd^{3+}) by KZnFC respectively. The increase uptake of ions by increasing the contact time is demonstrated the time-dependence. It is attributed to the availability of a large number of vacant surface sites during the initial stage and with the passage of time, as well as a high concentration gradient between the solution and the solid phase [4]. At the equilibrium time there is no further uptake that revealed that the saturated active site by sorbed ions under study. The affinity of amount sorbed ions onto mesoporous KZnFC follows the sequence: $Cs^{+} > Co^{2+} > Pb^{2+} > Ce^{3+} > Gd^{3+}$.

Fig. 7 Effect of pH on the sorption properties of (**a**) binary mixed $^{134}Cs^{+}$, $^{60}Co^{2+}$ and (**b**) individual Gd^{3+} and Ce^{3+} onto KZnFC



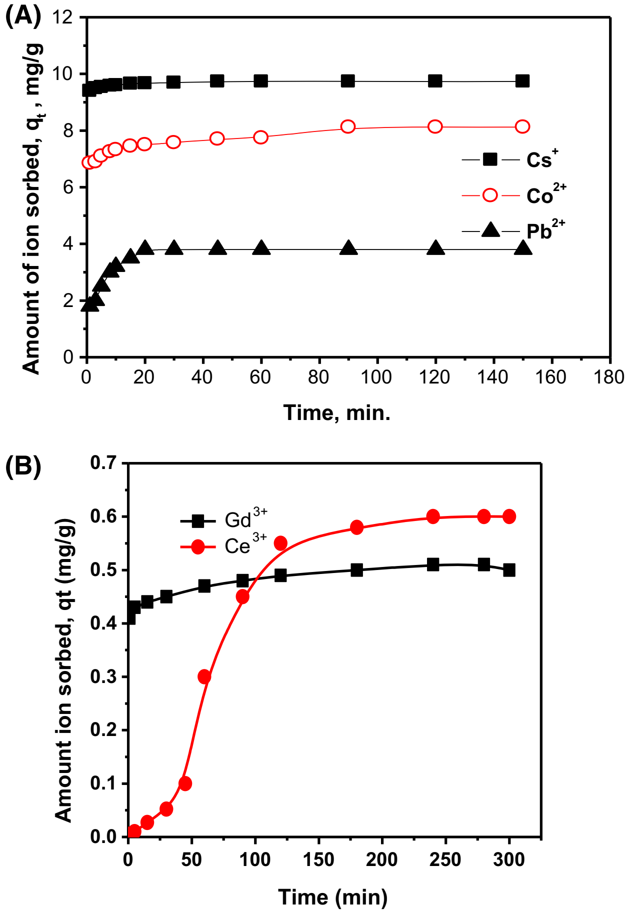


Fig. 8 Effect of contact time on the amount of ion sorbed of (**a**) $^{134}Cs^+$, $^{60}Co^{2+}$ and Pb^{2+} from 0.1 M HNO_3, (**b**) Gd^{3+} and Ce^{3+} from aqueous solution at pH 4.5 onto KZnFC

Effect of metal ion concentration

The effect of the investigated ions concentrations in the range 2–100 mg/L of Ce and Gd and 1–300 mg/L of $^{60}Co^{2+}$ and Pb^{2+} as well as 1–3000 mg/L of $^{134}Cs^+$ on the sorption onto KZnFC from nitric solution and aqueous solution were studied. The results obtained represented in Fig. 9 as a relation between the concentrations of the ions and the amount of ion sorbed. From this figure, the ions concentration in adsorbent increase with increasing its initial concentration in solution for all investigated ions. The increase in the uptake capacity of KZnFC with increasing initial ion concentration may be due to higher probability of collision between each investigated ion and KZnFC particles. The isotherm curves as seen in Fig. 9 are indicated that increase uptake of ions by increasing the initial ion concentration, it might be attributed to the availability of a large number of vacant surface sites onto KZnFC till saturation with sorbed metal ions. The results indicated that the maximum capacity of mesoporous KZnFC adsorbent are 170, 10.5, 3.88, 0.72 and 0.55 mg/g for $^{134}Cs^+$, $^{60}Co^{2+}$, Pb^{2+}, Ce^{3+} and Gd^{3+}, respectively.

Analysis of adsorption data

To understand the mechanism of sorption ions onto the prepared mesoporous KZnFC as nano adsorbent, the experimental data of $^{134}Cs^+$, $^{60}Co^{2+}$, Pb^{2+}, as example of sorbed ions for kinetic and isotherm analysis have been used.

Sorption kinetic studies

Sorption kinetics is controlled by various mechanisms such as mass transfer, diffusion control, chemical reactions, and particle diffusion. In order to clarify the kinetic characteristics of ions sorption under study onto ion exchanger, KZnFC from nitric solution, two well-known kinetic models namely; pseudo-first order and pseudo-second order kinetic models were calculated to evaluate experimental data.

Pseudo-first-order model

A pseudo-first-order model was used as reported by [30, 31]. The Lagergren first-order rat expression is written as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{4}$$

where q_e and q_t are the concentration of ion in the adsorbent at equilibrium and at time t, respectively (mg/g) and k_1 is the rate constant pseudo-first-order (min^{-1}). The relation between log ($q_e - q_t$) versus t was drawn as seen in Fig. 10, gives a straight line and the rate constants (k_1) and theoretical equilibrium sorption capacities, q_e, were determined from slopes and intercepts, respectively, and listed in Table 1. It is required that theoretically calculated equilibrium sorption capacities, q_e, should be in accordance with the experimental sorption capacity values. According to data in Table 1, although the linear correlation coefficients of the plots are good, the q_e (calculated) values are not in agreement with q_e (experimental) for all studied sorption processes. Therefore, it could suggest that sorption of these ions onto KZnFC is not a pseudo-first-order reaction.

Pseudo-second-order model

A pseudo second-order model is applied as reported by [32–34].

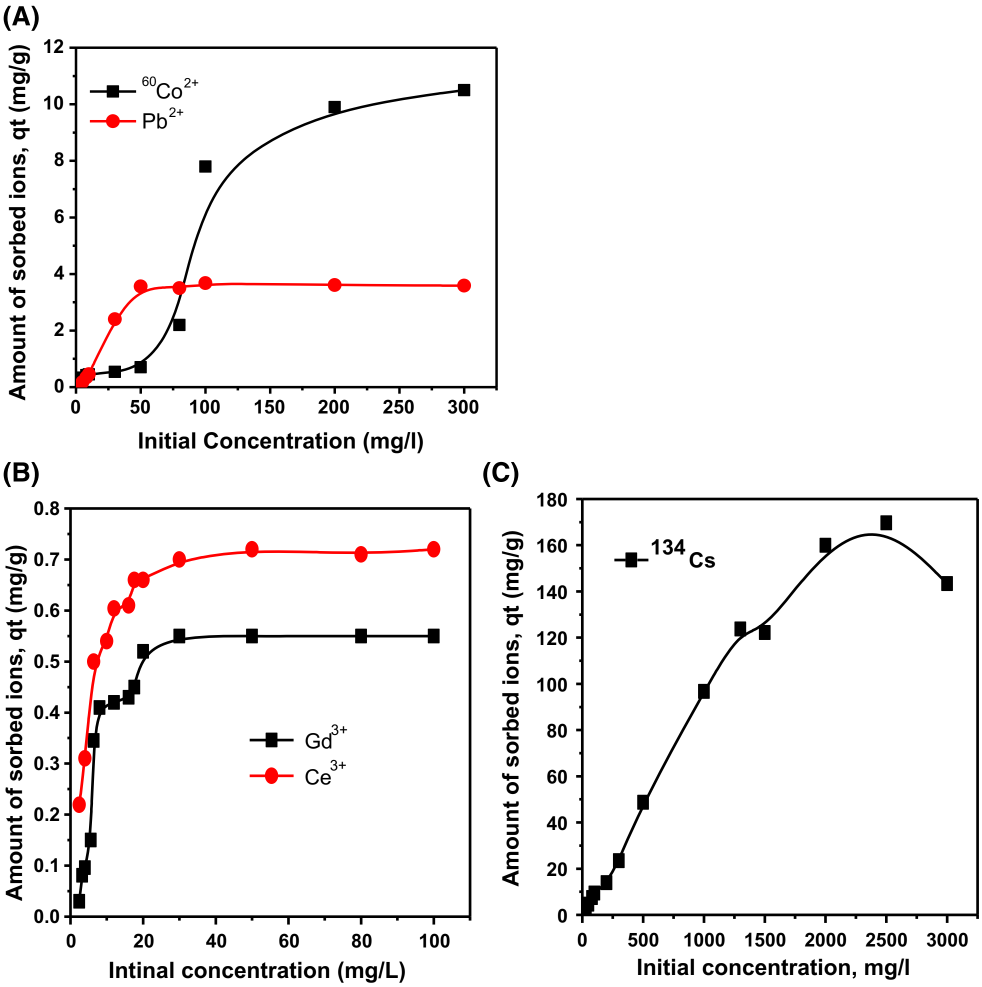


Fig. 9 Effect of initial concentration for (**a**) $^{134}Cs^{+}$, $^{60}Co^{2+}$ and Pb^{2+} from 0.1 M HNO_3, (**b**) Gd^{3+} and Ce^{3+} from aqueous solution at pH 4.5 on the amount sorbed onto KZnFC

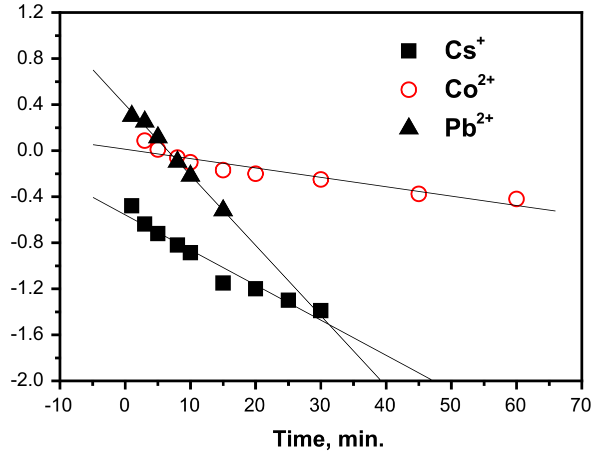


Fig. 10 Pseudo first-order kinetic plots for the sorption of $^{134}Cs^{+}$, $^{60}Co^{2+}$ and Pb^{2+} sorbed onto 0.1 g KZnFC 0.1 M HNO_3

Table 1 The calculated parameters of the kinetic model for Cs^{+}, Co^{2+} and Pb^{2+} ions sorbed onto KZnFC from 0.1 M HNO_3

Parameters	Ions under study		
	$^{134}Cs^{+}$	$^{60}Co^{2+}$	Pb^{2+}
q_e(exp) (mg/g)	9.73	8.12	3.8
Pseudo-first-order			
q_e (mg/g)	0.277	1.32	2.5
k_1 ($\times$ 10^{-2} min^{-1})	6.9	1.8	13.8
R^2	0.951	0.902	0.992
Pseudo-second-order			
q_e (mg/g)	10	7.8	3
k_2 ($\times$ 10^{-2}g/mg min)	16.6	20.0	9.6
h (mg/g min)	16.6	12.3	1.54
R^2	0.999	0.999	0.999

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{1}{q_e} t \tag{5}$$

where k_2 is the pseudo-second-order rate constant (g/mg × min).

The kinetic plots of t/q_t versus t for ^{134}Cs, ^{60}Co and Pb^{2+} sorption onto ion exchanger, KZnFC are represented in Fig. 11. The product $k_2 q_e^2$ is the initial adsorption rate represented as $h = k_2 q_e^2$ [32]. It can be shown that the h values for Cs^+ is higher than that for Co^{2+} and Pb^{2+}. The higher correlation coefficients (R^2) of the pseudo-second-order than the pseudo-first-order kinetic model is observed. Moreover, the calculated (q_e) are a consistent with experimental (q_e) values. Therefore, it could be deduced that sorption of ^{134}Cs, ^{60}Co and Pb^{2+} onto KZnFC described by the pseudo-second-order kinetic model.

Sorption isotherm

The amount of adsorbate onto the sorbent versus the concentration of adsorbate in the liquid at equilibrium is described adsorption isotherm process [35]. In this concern, the sorption removal isotherms of Cs^+, Co^{2+} and Pb^{2+} (in Fig. 9) from 0.1 M HNO_3 onto KZnFC were determined. The isotherms are regular, positive, and concave to the concentration axis. The initial fast sorption allows to reach equilibrium at higher ion concentrations within slow approach. These results reflect the efficiency of this ion exchange for removal of these ions from nitric acid concentrations especially for the Cs^+. Parameters of isotherm were calculated using Freundlich [36], as well as Dubinin-Radushkevich (D-R) [37] isotherm models.

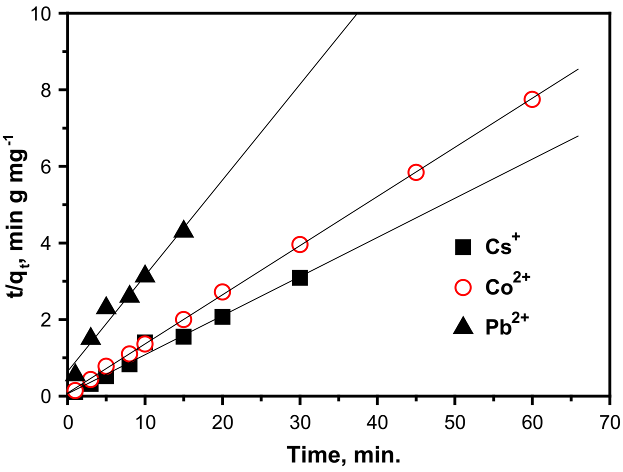


Fig. 11 Pseudo-second-order kinetic plots for the sorption of $^{134}Cs^+$, $^{60}Co^{2+}$ and Pb^{2+} from 0.1 M HNO_3 onto KZnFC

Freundlich isotherm model

The multilayer sorption and the sorption on heterogeneous surfaces are described by Freundlich model. The logarithmic shape of Freundlich equation is expressed as:

$$\log q_e = \log K_f + (1/n) \log C_e \tag{6}$$

where q_e is an amount of adsorbed ion per weight of adsorbent (mg/g), C_e is equilibrium concentration of metal ion in the equilibrium solution (mg/L), K_f is constant of the relative adsorption capacity of KZnFC (mg/g) and *1/n* is constant reflect the intensity for sorption process. The log q_e versus log C_e is represented in Fig. 12, which suggests that the sorption of Cs^+, Co^{2+} and Pb^{2+} ions onto KZnFC from nitric solution obeys Freundlich isotherm over the entire range of sorption concentration studied. The constants *1/n* and K_f numerical values are determined from slope and intercepts, respectively, as listed in Table 2. The numerical values of K_f represent sorption capacity of the ions under study loaded on KZnFC of a narrow sub-region having equally distribution energy sites towards metal ions. The value of (*1/n*) is dependent on sharing out the active sites of adsorbent material, strength and nature of sorption process. From Table 2 it can be observed that values of adsorption intensity (n) for Cs^+ and Pb^{2+} lies between 1 and 10 this indicating favorable sorption [38].

Dubinin-Radushkevich (D-R) isotherm model

D-R isotherm describes sorption on a single type of uniform pores. It is an analogue of Langmuir type [19]. The D-R isotherm is represented as follows:

$$\ln\ q_e = \ln\ q_m - \beta\varepsilon^2 \tag{7}$$

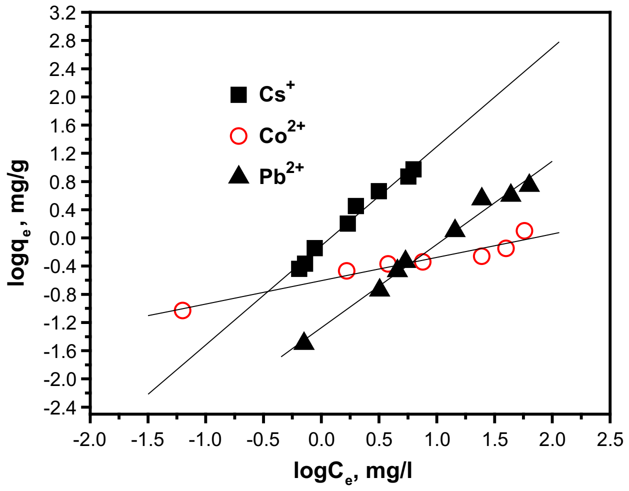


Fig. 12 Freundlich isotherm plots for the sorption $^{134}Cs^+$, $^{60}Co^{2+}$ and Pb^{2+} from 0.1 M HNO_3 onto KZnFC

Table 2 Freundlich and D-R isotherm isotherm parameters of Cs^+, Co^{2+} and Pb^{2+} ions sorbed onto KZnFC from 0.1 M HNO_3

Isotherm	Ions under study		
	$^{134}Cs^+$	$^{60}Co^{2+}$	Pb^{2+}
Freundlich isotherm			
$1/n$	1.4	0.33	1.18
K_f (mg/g)	0.773	0.247	1.27
R^2	0.990	0.997	0.993
D-R isotherm			
q_m ($\times 10^{-5}$ mol/g)	5	0.88	1.45
β (mol²/kJ²)	− 3.58	− 3.75	− 9.99
E (kJ/mol)	0.374	0.365	0.22
R^2	0.968	0.947	0.948

where q_m is the maximum sorbed amount of metal onto unit weight of ion exchanger i.e., sorption capacity (mg/g), β is a constant reflect to sorption energy (mol²/kJ²); and $\varepsilon = RT\ln(1 + 1/C_e)$, ε is the Polanyi potential where R is the gas constant (kJ/mol × K), and T is absolute temperature (K).

The free energy (E) of sorption is calculated from:

$$E = \frac{1}{\sqrt{2\beta}} \tag{8}$$

The values of E can be related to the reaction mechanism. If E of 8–16 kJ/mol, sorption is controlled by ion exchange [5]. In case of $E < 8$ kJ/mol, sorption mechanism might be affected by physical forces. The D-R plots of $\ln q_e$ versus ε^2 for sorption of ions onto KZnFC nitric solution are given in Fig. 13. The data revealed that the D-R isotherm expression is followed for each metal ion. Linear regression analysis using paired of $\ln q_e$ and ε^2 resulted in the derivation of q_m, β, E and the R^2. These D-R parameters, evaluated for sorption of the investigated ions in nitric solution, are listed in Table 2. The maximum sorption capacities of this ion exchange (q_m) are (5, 0.88 and 1.45) × 10^{-5} mol/g for Cs, Co and Pb respectively. The values of the mean free energy, E, of sorption of the ions under study onto KZnFC from nitric solution are < 8 kJ/mol, which are within the energy ranges of physical sorption mechanism.

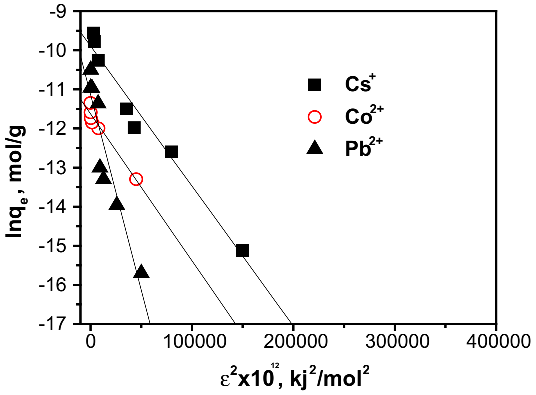


Fig. 13 D-R isotherm plots for the sorption of $^{134}Cs^+$, $^{60}Co^{2+}$ and Pb^{2+} ions sorbed onto KZnFC from 0.1 M HNO_3

Compression between different materials

The efficiency recovery characteristic of prepared nano particles of KZnFC towards some ions and/or radionuclides are evaluated. The obtained results are compared with the available literature data as represented in Table 3. These comparison are revealed that the KZnFC a promising nano adsorbent material for efficient and economical for wastewater treatment.

Sorption mechanism

The sorptive removal of ions ($^{137,134}Cs$, ^{60}Co, Pb^{2+}, Ce^{3+} and Gd^{3+}) under study using a KZnFC material is investigated. A relative selectivity uptake of $^{134}Cs^+$ as mono valvent metal ions (M^+) rather than the other metal ions (M^{n+}) of $^{60}Co^{2+}$, Pb^{2+}, Ce^{3+} and Gd^{3+} using nanoparticles of KZnFC might be attributed to cation exchange mechanism as represented by the following

$$M^+ + KZn[Fe(CN)_6] \rightarrow MZn[Fe(CN)_6] + K^+ \tag{9}$$

$$M^{2+} + 2KZn[Fe(CN)_6] \rightarrow M\{Zn[Fe(CN)_6]\}_2 + 2K^+ \tag{10}$$

$$M^{3+} + 3KZn[Fe(CN)_6] \rightarrow M\{Zn[Fe(CN)_6]\}_3 + 3K^+ \tag{11}$$

The experimental results demonstrate that the selectivity takes the following order: $^{134}Cs^+ > ^{60}Co^{2+} > Pb^{2+} > Ce^{3+} > Gd^{3+}$. This may be related to the hydrated ionic radius. The anion part of the KZnFC ion exchanger is being larger in size and possessing low charge density, it could be considered as 'soft base' [18]. Thus the metal ion present in the hydrated form that arranged in order of the increasing ionic size have followed the obtained selectivity order of ion exchange except Co^{2+}. It is indicated that the smallest hydrated ionic size of ions under study would reduce charge to size ratio and enhancement of the 'soft acid' behavior going from Co^{2+} (highest hydrated ion size) to Cs^+ (lowest hydrated ionic size). This indicated that increasing extent of Cs^+ and most favorite for the exchange with K^+ ions of KZnFC nanoparticle ion exchanger.

Table 3 Adsorption capacity of Cs^+ and Co^{2+} by different adsorbent materials

Material	Adsorption capacity (mg/g)		References
	Cs	Co	
Poly (acrylic acid–maleic acid)SiO_2/Al_2O_3	16.0	NR	[2]
Nickel hexacyanoferrate–walnut shell	4.94	NR	[39]
Polyacrylonitrile–potassium nickel hexacyanoferrates composite	157.7	NR	[40]
Prussian blue-coated magnetic nanoparticles	96	NR	[41]
Prussian blue caged in alginate/calcium beads	131.57	NR	[42]
Prussian blue caged in alginate/calcium beads reinforced with carbon nanotubes	142.85	NR	[42]
Prussian-blue-modified magnetite (PB–Fe_3O_4)	16.2	NR	[43]
Copper ferrocyanide functionalized mesoporous silica	17.1	NR	[44]
Kaolin	NR	0.56	[45]
Hectorite particles	NR	2.65	[45]
Roasted date pits	NR	6.28	[45]
Hazelnut shells	NR	13.88	[45]
Lewatit resin	NR	21.98	[46]
Lemon peel	NR	22.0	[47]
ZrO–montmorillonite	NR	22.8	[47]
Industrial waste	NR	35.0	[47]
Almond green hull	NR	45.5	[47]
Marble	2.37	2.24	[48]
Impregnated polymer [P(AM-AA-AN)-DAM/DtBB18C6]	58.7	94.4	[49]
Mesoporous KZnFC	170	10.5	This work

Another mechanism of complex or chelate of metal ions under study with incorporation KZnFC material is suggested [39]. The high affinity to Co^{2+} with higher hydrated ionic radius than Pb^{2+} and Ce^{3+} this may be attributed to that zinc hexacyanoferrate(II) species their derivatives exist as octahedral $[Fe(CN)_6]^{-4}$ units linked to tetrahedral Zn^{2+} ions, leading to hexagonal bipyramidal cages which are capable of encapsulating Cs^+ [50] and hydrated $Co^{2+}(d^7)$ have octahedral configuration [51]. It might be also, the higher selectivity towards Cs^+ is due to its porous cubic structure with a channel diameter of about 3.2 Å, which is permeable to ions with a small stokes radius such as Cs^+, K^+, and Cl^-. The hydrated Ln^{3+} ions have basic tricapped trigonal prismatic structure in aqueous solution [52] that reflect low fitting with structure of KZnFC nanoparticle material.

Conclusion

A mesoporous particle of KZnFC material has been prepared and characterized as well as their sorption characteristic towards some fission products and toxic heavy metal from binary and/or mono system have been investigated. The sorption results, of ^{134}Cs, ^{60}Co, Pb^{2+} and lanthanides ions showed that KZnFC is an efficient sorbent material for removal of ^{134}Cs, ^{60}Co and pb^{2+} ions from nitric solution. The affinity of lanthanides sorption onto KZnFC is reported from aqueous solution at pH 4.5. It can be concluded that the sorption performance of a mesoporous particle of KZnFC not only for $^{137,134}Cs$ but also other fission products (^{60}Co, lanthanides), toxic heavy metal (Pb^{2+}). It is also deduced that a selective separation between these five ions under study could be achieved on different media (aqueous and/or nitric acid solutions). After comprehensive study, it is revealed that the prepared mesoporous particles of KZnFC is recommended and promising for efficient and economic decontamination of radionuclides, toxic metals either from liquid radioactive waste or contaminated wastewater. The adsorption equilibrium process of $^{134}Cs^+$, $^{60}Co^{2+}$ and Pb^{2+} obeyed the Freundlich and D-R adsorption isotherms. This suggests that some heterogenity in the surface or pores of KZnFC will play a role in the metal ion sorption. The kinetics of adsorption of $^{134}Cs^+$, $^{60}Co^{2+}$ and Pb^{2+} by KZnFC follow the second-order kinetic model.

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