

SUMMARY AND CONCLUSION

Sorption of both radionuclides and organic ingredients onto solid sorbents is one of the most important ways in processing the aqueous wastes generated from nuclear activities for both inorganic and organic ingredients.

The radioactive waste solutions contain chemicals mainly used in decontaminating processes at nuclear activities. The selected contaminants used are ^{134}Cs , ^{89}Sr and ^{60}Co in addition to phenol. So, the current work in this thesis is directed to specify natural materials having high sorption affinity and low economic cost to be used in recovering the selected contaminants from radioactive waste solutions. For this objective, the samples considered are two types of unmodified clay samples (*one from South-West of Allamine, Egypt and has a notation S_1 and the second from Baharia oasis, Egypt and has a notation S_2*) and a commercial activated granular carbon sample (*from Aldrich company, and has a notation of S_3*). The other objective is devoted to determine the adsorption capacity of the studied samples to the selected contaminants. This work also is concerned with the sorption behavior of ^{134}Cs , ^{89}Sr , ^{60}Co and phenol onto the samples under various conditions, as well as the characterization of the investigated samples.

The experimental results are in the form of batch technique. Column investigations were used to identify the applicability of these sorbents for radioactive waste solutions treatment. The basic methodology used involved making standard solutions; mixing a fixed amount of adsorbent (clay or carbon) with specific volume of solution; and then allowing the mixture to equilibrate for definite time. From the concentration of equilibrium solution and the mother solution the amount adsorbed of the contaminant can be determined.

This thesis consists of three chapters summarized as follows:-

Chapter (I)

This chapter comprises a review on the major groups commonly found in clay minerals especially aluminosilicates, oxides and organic matter. It deals with the electrochemical properties of clay-surface such as permanent charge, variable charge and point of zero charge as well as short account about specific surface area and surface charge of clay. Activated carbon is one of carbonaceous materials so in this chapter the light focused on the origin, sources, surface area, and surface chemistry of activated carbon as well as its importance. Due to the importance of liquid to solid ratio (V/m) for determining the extent of the interaction of two phases, a brief dissection dealing with it has been included. The chapter contains also a brief account on the sorption phenomena, kinds of adsorption, adsorption isotherms and adsorption characteristics (evaluation of the adsorption and quantitative descriptions of adsorption). Finally; it has a short account about nuclear, chemical and environmental characteristics of the considered contaminants.

Chapter (II)

This chapter contains a detailed description of chemicals, sampling and the instrumentation utilized in this work. It deals with collection and preparation of the investigated samples (S_1 , S_2 and S_3), in addition to preparation and characterization of the contaminants (^{134}Cs , ^{89}Sr , ^{60}Co and phenol). It includes the experimental techniques used in sorption of the representative contaminants onto the considered samples and the factors affecting sorption process. Finally, it includes short notes about desorption study of the contaminants from the loaded samples and short notes about column technique investigations.

Chapter (III), result and discussions:

This chapter reveals the experimental results of some physical and chemical characteristics of the studied samples (S_1 , S_2 and S_3) as well as the mineralogical composition of the investigated clays. It includes the experimental results of sorption affinity of sorbents to the considered contaminants (^{134}Cs , ^{89}Sr , ^{60}Co and phenol) at different conditions. Also, it has the desorption results of the selected contaminants loaded on the studied samples. Finally this chapter includes the experimental results obtained from column investigations. The experimental results can be summarized as follows:-

Some properties of the studied samples are as follows:-

- The moisture content (in percent) of the sorbent samples is 4.5%, 5.1% and 1.3% for S_1 , S_2 and S_3 , respectively.
- Specific surface area of sorbent samples is $407 \text{ m}^2 \text{ g}^{-1}$, $350 \text{ m}^2 \text{ g}^{-1}$ and $610 \text{ m}^2 \text{ g}^{-1}$ for S_1 , S_2 and S_3 , respectively.
- Point of zero charge (PZC) of the sorbent samples of S_1 , S_2 and S_3 is 5.8, 6.2 and 6.5, respectively, and this means that their surface will therefore be negatively charged and have an electrostatic affinity for Cs^+ , Co^{2+} , and Sr^{2+} from aqueous solutions when the pH of the ambient solution is greater than estimated value of the sorbent.
- The total exchangeable metallic cations (TEMC) of S_1 and S_2 are 95 (meq/100g) and 41 (meq/100g), respectively.
- The mineralogical composition of the investigated clay samples obtained from X-ray diffraction (XRD) reveals that the S_1 has smectite as a predominant mineral and the mixed layer of illite/smectite as the most abundant. S_1 has a small fraction of gypsum. Moreover, S_2 has siderite and feldspars as well as calcite as abundant minerals. Kaolinite, calcite and dolomite are present in S_2 .

- The chemical analysis of the investigated clay samples reveals that the concentration of Al in S₁ is higher than that in S₂. The concentration of Ca in S₂ is greater than that in S₁. The concentration of Fe in S₂ is higher than that in S₁.
- The elemental analysis of activated carbon shows that the numerical ratios of the main constituent atoms (C, H and O) are 4:3:1 and this reveals that the activated carbon is hydrophilic. Also, the O/C ratio is being 0.24 which reveals that the activated carbon has a predominant content of acidic surface centers and H/C ratio is being 0.70 which implies that the surface has aromatic nature.

The experimental results of sorption processes:

The sorption affinity of Cs⁺, Co²⁺, and Sr²⁺ ions onto the studied samples (S₁, S₂ and S₃) is affected by the volume weight ratios (V/m), contact time, pH of the aqueous phase, competing ion concentration and metal ion concentration.

- The volume weight ratios (V/m) sufficient for the quantitative removal of the ions and phenol from aqueous waste solutions using considered samples are as follows: for the representative ions and clay is 0.200 L g⁻¹ for the representative ions and activated carbon is 0.250 L g⁻¹ for phenol and clay being 0.014 L g⁻¹ and for phenol and activated carbon is 0.016 L g⁻¹.
- The experimental results reveal that the amount sorbed of metal ion increases with time, till it attains constant value depending on the type of the adsorbate and the nature of the sorbent. The sorption was initially increased rapidly, but then the process slows down and subsequently attains a constant value within 50, 60, and 60 min for Cs⁺, Sr²⁺ and Co²⁺ ions, respectively i.e., when adsorption equilibrium is established. The same trend is observed for sorption of phenol onto the investigated sorbent samples and the equilibrium attained within 40 min for activated carbon and within 60 min for both S₁ and S₂. The variation of amount of sorbed values of the selected contaminants depends on the surface area

of the grains, the mineralogical and the chemical composition of each sorbent sample. The removal of Cs^+ , Sr^{2+} and Co^{2+} ions in addition to phenol from aqueous solutions by S_1 , S_2 and S_3 described as a four step process: bulk solution transport, film diffusion transport, pore transport and adsorption.

- Lagergren equation was applied for studying the kinetics of sorption of the selected radionuclides and phenol onto the studied samples, and the obtained linear plots indicate the applicability of the equation for sorption of all contaminants onto the investigated samples. Kinetically the sorption is first order reaction. The rate constant (K_{ad}) values for Sr^{2+} , Co^{2+} and Cs^+ for S_1 are 0.0488, 0.0525 and 0.0519 min^{-1} , respectively. The K_{ad} values of Sr^{2+} , Co^{2+} and Cs^+ for S_2 are 0.0244, 0.0366 and 0.0403 min^{-1} , respectively. The K_{ad} values of Sr^{2+} , Co^{2+} and Cs^+ for S_3 are 0.0541, 0.052 and 0.0711 min^{-1} , respectively. The K_{ad} values of sorption phenol are 0.0403, 0.0451 and 0.1543 min^{-1} for S_1 , S_2 and S_3 , respectively.
- The hydrogen ion concentration is one of the most important factors influencing the adsorption of the contaminants from aqueous solutions onto the investigated samples. The experimental data reveal that the contaminant amount sorbed increase with increasing the pH until a maximum uptake of Cs^+ , Co^{2+} , Sr^{2+} at certain pH and with a further increase in pH values the amount sorbed falls gradually. In strongly acidic medium the amount sorbed of the radionuclides by the investigated samples are very small or negligible. This was discussed in the light of competing effect of hydrogen ion. At higher pH values, the amount sorbed of ^{134}Cs , ^{60}Co and ^{89}Sr shows a gradual increase with increasing the pH with a maximum value and then sharply decrease until pH 9. This decrease in the amount sorbed may be attributed to the amphoteric character of the sorbents. The maximum amount sorbed of the selected ions onto both S_1 and S_2 is around a pH of 7.2, 7.5 and

6.2, ± 0.2 for Cs^+ , Co^{2+} and Sr^{2+} , respectively. The maximum sorption of the selected ions onto S_3 sample is around a pH of 7.6, 7.2 and 6.5, ± 0.2 for Cs^+ , Co^{2+} and Sr^{2+} , respectively. The experimental sorption data represented as a relation between distribution coefficient (K_d) and $\text{Log} [\text{H}^+]$ for sorption of Cs^+ , Co^{2+} and Sr^{2+} from aqueous solution onto the investigated samples reveal a deviation from the ideal sorption and therefore the mechanism is not pure ion exchange mechanism and other mechanisms may be present. This attributed to the complexity of the systems involving sorption and thus the possibility of sharing of more than one mechanism in the sorption process is present.

- The maximum adsorption capacity of phenol onto S_1 at around a pH ranging between 7.5 and 8.1, onto S_2 at around a pH ranging between 7.3 and 7.9, and onto S_3 at around a pH ranging between 5 and 6.4. At higher pH values ($\text{pH} > 8.1, 7.9$ and 6.4), an important decrease of the amount sorbed was observed likely due to the increase of the concentration of the ionized form, of phenol, which is adsorbed to a lower extent because of its higher solubility in water. On the other hand, at $\text{pH} < 7.5, 7.3, 5$, the adsorption capacity also lightly diminishes with respect to that at pH_{max} for the investigated samples.
- The experimental results of isotherm in the form of batch indicate that Freundlich equation has been fitted to the sorption affinity of the selected contaminants onto the studied samples for the concentration range used, as follows:
 - For sorption of Cs^+ ions onto S_1, S_2 and S_3 , the Freundlich parameters are $K_F = 17.49 \text{ mg g}^{-1}, 6.11 \text{ mg g}^{-1},$ and 1.7 mg g^{-1} , respectively, and $1/n$ are 1.60, 0.92 and 1.97, respectively. This indicates that the uptake of Cs^+ from aqueous solutions is lower and S_1 has more capacity for Cs^+ ions than that of both S_2 and S_3 samples.

- For sorption of Co^{2+} ions onto S_1 , S_2 and S_3 , the Freundlich parameters are $K_F = 20.79 \text{ mg g}^{-1}$, 21.69 mg g^{-1} , and 14.7 mg g^{-1} , respectively, and $1/n = 1.39$, 1.32 , and 4.42 , respectively. This indicates that S_2 and S_1 are nearly similar and they are better than S_3 sample for the uptake of Co^{2+} from aqueous solutions.
- For sorption of Sr^{2+} ions onto S_1 , S_2 and S_3 , the Freundlich parameters are $K_F = 22.28 \text{ mg g}^{-1}$, 19.68 mg g^{-1} , and 6.1 mg g^{-1} , respectively, and $1/n = 1.34$, 1.53 , and 2.54 , respectively. This indicates that S_1 is the best sample for the uptake of Sr^{2+} from aqueous solutions.
- For sorption of phenol onto S_1 , S_2 and S_3 , the Freundlich parameters are $K_F = 3.80 \text{ mg g}^{-1}$, 2.50 mg g^{-1} , and 17.4 mg g^{-1} , respectively, and $1/n = 3.64$, 3.92 and 8.44 , respectively. This indicates that S_3 is the best sample for the uptake of phenol from aqueous solutions.
- The effect of changing the competing cation concentration on sorption of ^{134}Cs , ^{89}Sr and ^{60}Co by the investigated samples was investigated. Two competing cations were used for every selected radioelement. The obtained results show that sorption of Cs^+ ions was reduced in presence of either K^+ or Ba^{2+} ions as competing cations, and also presence of either K^+ or Ca^{2+} ions decreases the amount sorbed of Sr^{2+} ions, also presence of either Mg^{2+} or Fe^{3+} ions decreases the amount sorbed of Co^{2+} ions onto the investigated sorbent samples.
- The competing effect of both K^+ and Ba^{2+} ions for sorption of Cs^+ ions is reported as follows: As K^+ ions concentration increased up to 50 mg L^{-1} , the amount sorbed of Cs^+ ions decreased from 17.4 mg g^{-1} to 8.4 mg g^{-1} , from 6.1 mg g^{-1} to 3.25 mg g^{-1} , and from 1.7 mg g^{-1} to 0.52 mg g^{-1} for sorbent samples S_1 , S_2 and S_3 , respectively. As Ba^{2+} ions concentration increased up to 50 mg L^{-1} , the amount sorbed of Cs^+ ions decreased from 17.4 mg g^{-1} to 6.0 mg g^{-1} , from 6.1 mg g^{-1} to 2.16 mg g^{-1} , and from 1.7 mg g^{-1} to 0.37 mg g^{-1} for sorbent samples S_1 , S_2 and S_3 ,

respectively. These results may be attributed to similarity of the ionic radii of K^+ , Ba^{2+} and Cs^+ ions. It is noticeable also that Ba^{2+} is better than K^+ ion of the competition. This reported due to the ionic potential of these ions.

- The competition effect of both K^+ and Ca^{2+} ions for sorption of Sr^{2+} ions is reported as follows: As K^+ ions concentration increased up to 50 mg L^{-1} , the amount sorbed of Sr^{2+} ions decreased from 22.3 mg g^{-1} to 11.03 mg g^{-1} , from 19.6 mg g^{-1} to 7.86 mg g^{-1} , and from 6.1 mg g^{-1} to 3.5 mg g^{-1} for sorbent samples S_1 , S_2 and S_3 , respectively. As Ca^{2+} ions concentration increased up to 50 mg L^{-1} , the amount sorbed of Sr^{2+} ions decreased from 22.3 mg g^{-1} to 8.09 mg g^{-1} , from 19.6 mg g^{-1} to 5.22 mg g^{-1} , and from 6.1 mg g^{-1} to 2.6 mg g^{-1} for sorbent samples S_1 , S_2 and S_3 , respectively. These results indicate that both K^+ and Ca^{2+} have a completion effect on sorption of Sr^{2+} . This may be attributed to similarity of the ionic radii of K^+ , Ca^{2+} and Sr^{2+} ions. Although the ionic radii of K^+ and Sr^{2+} are closed similar than that of Ca^{2+} and Sr^{2+} it was noticed that Ca^{2+} is better than K^+ ion for competition of Sr^{2+} . This could be attributed to their ionic potential (Z^n/r) and the fact that the Ca^{2+} and Sr^{2+} cations have chemical properties similar to each other and have similar chemical charges.
- The competition effect of both Mg^{2+} and Fe^{3+} ions for sorption of Co^{2+} ions is reported as follows: As Mg^{2+} ions concentration increased up to 50 mg L^{-1} , the amount sorbed of Co^{2+} ions decreased from 20.7 mg g^{-1} to 7.09 mg g^{-1} , from 21.7 mg g^{-1} to 4.84 mg g^{-1} , and from 14.7 mg g^{-1} to 9.93 mg g^{-1} for sorbent samples S_1 , S_2 and S_3 , respectively. As Fe^{3+} ions concentration increased up to 50 mg L^{-1} , the amount sorbed of Co^{2+} ions decreased from 20.7 mg g^{-1} to 5.14 mg g^{-1} , from 21.7 mg g^{-1} to 3.28 mg g^{-1} , and from 14.7 mg g^{-1} to 8.72 mg g^{-1} for sorbent samples S_1 , S_2 and S_3 , respectively. These results indicate that both Mg^{2+} and Fe^{3+}

- In column investigations, the S-shape breakthrough curves in sorption of the selected contaminants from aqueous solutions onto the studied samples are obtained. It was found that the maximum capacity of the selected contaminants onto the studied samples using a small scale column (1cm internal diameter and 50 cm height) packed with either 4 g of granular activated carbon or 5 g of clay sample, under the conditions of the experiment are as follows:
 - The maximum capacity of Cs^+ ions onto S_1 , S_2 and S_3 is 14.4 mg g^{-1} , 7.2 mg g^{-1} and 1.7 mg g^{-1} , respectively.
 - The maximum capacity of Co^{2+} ions onto S_1 , S_2 and S_3 is 19.6 mg g^{-1} , 21.0 mg g^{-1} and 14.7 mg g^{-1} , respectively.
 - The maximum capacity of Sr^{2+} ions onto S_1 , S_2 and S_3 is 20.8 mg g^{-1} , 15.6 mg g^{-1} and 6.1 mg g^{-1} , respectively.
 - The sorption capacity of phenol onto S_1 , S_2 and S_3 is 3.4 mg g^{-1} , 2.2 mg g^{-1} and 16.5 mg g^{-1} , respectively. These data show the effectiveness of the samples for removal of the selected contaminants from aqueous solutions.

Finally, the major finding of this work is that the clay sample S_1 is the best for removal Cs^+ ions from aqueous radioactive waste solutions. The two clay samples (S_1 and S_2) have good sorption capacities and a rapid sorption rates for both Co^{2+} and Sr^{2+} ions at the given conditions. The activated carbon sample (S_3) has greater adsorption capacity to phenol in comparison to the two untreated clay samples (S_1 and S_2).