Summary

The work in this thesis is directed to make use of novel sorbents prepared from agro-residue (Rise Husk, RH) in separation and recovery of non-radioactive analogous (Zn^{+2} and Cd^{+2}) from waste constituents which is similar to that waste of Egypt's Cyclotron radioisotopes production units (^{67}Ga and ^{111}In), respectively. This thesis is divided into four main chapters:

Introduction: This chapter gives a literature survey on the importance of radioisotopes for medical applications, the properties that take into consideration in choice of these isotopes and the kinds of radioisotopes produced in different types of cyclotrons. The structure of Egypt's Cyclotron and target systems for production of (^{67}Ga and ^{111}In) radioisotopes were described in details. The most important techniques that are used in the recovery process such as: solvent extraction and ion exchanger were summarized. Moreover, adsorption was discussed in details. In this concern, the survey includes the causes and types of adsorption, factors influencing adsorption process (e.g. equilibrium time, metal type, adsorbent weight, initial concentration, surface loading, sorbent type and pH) adsorption isotherms, contacting systems and modes of operations. In addition to the new materials used in manufacturing of activated carbons as well as the surface chemistry of the produced activated carbons.

Experimental: This chapter gives the procedures used for preparation of two series of sorbents (i) one step steam activated carbons from alkaline treated RH and (ii) silica extracted from RH by alkaline treatment. Also the experiments used in surface characterization of prepared sorbents: adsorption from gas phase (estimation of surface area by nitrogen adsorption) and adsorption from the liquid phase (methylene blue test, iodine number and phenol number) are given.

The procedures used to show the physicochemical characterization of prepared sorbents (e.g. density, scanning electron microscopy (SEM), adsorbent pH; CHN analysis and ash content) were illustrated in details.

The potential use of prepared sorbents for adsorption of zinc, cadmium and nickel in batch mode was investigated using atomic absorption spectrometry. The factors affecting the sorption process (e.g. equilibrium time, sorption medium type, sorption medium molarity and pH) were examined for all metal ions under investigations. Adsorption isotherm of each system was determined and the two-parameters equilibrium adsorption models (Langmiur, Freundlich and Dubinin-Radushkevich) were applied. The magnitude of the interactions has been made in batch experiments of binary component systems (Zn-Ni) and (Cd-Ni) using Langmiur model for competitive adsorption.

The column performance parameters of the two binary component systems (Zn-Ni) and (Cd-Ni) were determined. In this concern, several parameters were studied include solution flow rate and bed depth. The bed-depth service time (BDST) has been applied on (Zn-Ni) and (Cd-Ni) column data. Finally, recovery of Zn^{+2} and Cd^{+2} were occurred by the two modes of operation: the batch and column modes and the recommended procedures were described.

Mathematical treatment of experimental results:

This part includes all the mathematical equations used for calculation of the various constants required to explain the experimental data.

Results and discussion: This chapter includes the results and discussion of the experiments, it is divided into three parts:-

Part (A): describes the physicochemical and adsorptive properties of the prepared sorbents. In this concern, the packed density have the same order of the apparent density. The packed densities are approximately 3 folds the apparent density of natural Rice Husk (RH), in general, with the lowest value for alkaline treated RH and highest value for the silica extracted from RH using KOH. The values of the ash content of the silica extracted from Rice Husk by KOH at different concentrations, are always higher than that of the steam activated carbons, as these samples contain metal oxides beside the high content of silica. The BET surface areas of the prepared sorbents take the order that: RP-5>RP-1>RS-5 (S_{BET} for RP-1=204 m^2/g, RP-5=480 m^2/g and RS-5=13 m^2/g). The SEM photograph shows progressive changes in the surface of the sorbents. In original Rice Husk (RH) the outer membrane was found to be cellulose much filled up with silica. A sample prepared from steam pyrolysis (RP-5) takes the same regular rows of fiber skeleton of the original Rice Husk, the skeleton is empty from silica. Whereas, sample of silica extracted from Rice Husk shows different shapes of different sizes and gives an irregular amorphous surface. On studying the porosity characteristics of the various sorbents, Surface areas of the first group of sorbents (RP-1, RP-2 and RP-5), steam activated carbons from alkaline treated Rice Husk, range between 200 and 500 m^2/g, while the surface areas of second group of sorbents (RS-1, RS-2 and RS-5) range between 10 and 110 m^2/g. Adsorption tests from aqueous phase show that, the first group of sorbents has good capacity for removing of iodine more than the second group.

Whereas, the second group of sorbents has no affinity to the uptake of either phenolic compound (phenol or ρ-nitrophenol). The different kinds of sorbents show different affinities for methylene blue uptake and also different patterns of adsorption.

Part (B): It includes the sorption behavior of selected metal ions (Zn^{+2}, Cd^{+2} and Ni^{+2}) in single and two-component systems using novel sorbents prepared from Rice Husk in the two modes of operation: batch and column.

The first section in this part is devoted to the uptake behavior of the three single systems: RS-5: Zn^{+2}; RS-5: Cd^{+2} and RS-5: Ni^{+2}. Factors affecting the equilibrium time of each adsorption system is determined onto different sorbents using two different sorption mediums (NH_4Cl and HCl) at various sorption medium molarities (0.01, 0.1 and 1M). The data show that the best sorption medium molarity in case of Zn^{+2} and Ni^{+2} is 0.01M NH_4Cl and the best sorption medium molarity in case of Cd^{+2} is 5M HCl using sorbent RS-5.

In this concern, the adsorption equilibrium takes place within 15 min. for Ni^{+2} onto sorbent (RS-5) with sorption medium molarity 0.01M NH_4Cl (i.e. fast kinetic) compared to equilibrium steady state conditions for Zn^{+2} and Cd^{+2} onto sorbent RS-5 (equilibrium time takes place after 8 h in case of Zn^{+2} with sorption medium sorption medium molarity 0.01 M NH_4Cl, while the equilibrium time of Cd^{+2} reaches after 5 h of shaking with sorption medium molarity 5.00 M HCl).

The effect of pH showed that the adsorption of all the metal ions studied was markedly influenced by the solution pH. There was a rapid increase in metal ion adsorption on increasing acid molarity (decrease pH) and the adsorption decreased as the molarity of NH_4Cl increased. In this concern, the distribution coefficient K_d of the three ions (Zn^{+2}, Cd^{+2} and Ni^{+2}) versus pH gave a straight lines indicating an ion exchange mechanism may be occurred. This can be explained on the basis of silica which exists in significant quantities (94 % from the ash content) according to elemental analysis of RS-5. The surface hydroxyl groups of silica (silanol and disilanol groups) can function as donors of a proton and a hydroxyl, forming negative and positive sites on the surface respectively. Hence, when silica is brought in contact with metal solutions both cation and anion exchange can take place, the former being favored at higher pH and the latter at lower pH. As well as the carbon content (37 %) is responsible for adsorption of metal ions on the surface either by covalent or hydrogen bonding. So, the presence of silica and surface containing oxygen functional groups are responsible for the metal uptake using ion exchange and/or metal complex formation.

Kinetic studies using different sorbents (RP-1, RP-5 and RS-5) in different sorption medium type (NH_4Cl and HCl) at varies sorption medium molarities (0.01, 0.1, 1M) indicate that Zn^{+2} and Cd^{+2} adsorption systems obey the Lagergren first order with average rate constant (K_d ~ 0.28 h^{-1}).

Whereas, (Ni^{+2} : RS-5) adsorption system obeys the second order with average rate (K_d ~ 0.62 g mg^{-1} $min.^{-1}$). The intraparticle diffusion rate constant for different metal ions represented by K_p follows the following order Cd^{+2}>Zn^{+2}>>Ni^{+2}. The values of pore diffusion coefficients for Zn^{+2}, Cd^{+2} and Ni^{+2} are in the order of 10^{-11} cm^2 s^{-1} indicating that the rate-controlling step is intraparticale diffusion.

The values of mass transfer coefficients indicate that the velocity of adsorbate transport from the bulk to the solid phase is faster in case of Zn^{+2} compared to that of Cd^{+2}. The effect of sorption medium molarity shows a slight difference in mass transfer coefficient but the sorbent type affects the mass transfer coefficient in the order RS-5>RP-1>RP-5. However, the mass transfer model in case of Ni^{+2} is not applicable at any parameter under study because of the small initial concentration (10 ppm) used.

It was found that the adsorption in single component systems for all selected metal ions fit the two parameters isotherms models (Langmiur, Freundlich and Dubinin-Radushkevich). Finally, the value of energy as indicated by the Dubinin-Radushkevich constant E is in the range of 8-16 kJ $mole^{-1}$ which is expected for physical sorption reaction.

In the second section, the competitive adsorption of the two binary systems (Zn-Ni) and (Cd-Ni) depends entirely on the solution pH and the equilibrium time. This observation can be explained on the basis of the fast kinetics of Ni^{+2} (15 min.), compared to Zn^{+2} and Cd^{+2} (8 h for Zn^{+2} and 5 h for Cd^{+2}, respectively). The uptake values of Zn^{+2} in presence of constant concentration of Ni^{+2} (10 ppm) (i.e. in the binary system) is lower than that of Zn^{+2} in (single system), this is according to the competitive effect. Similar trend can be observed in case of (Cd-Ni) binary system. The Langmuir model for competitive adsorption was applicable and an attempt was made to describe the adsorptive behavior of the substrates under investigations for two-component systems .

The third section shows the continuous-column mode experiments of binary systems (Zn-Ni) and (Cd-Ni) which were examined by small column test using (RS-5). It was found that, by reducing the flow rate, the service time increased and hence the volume of the solutions effectively increased. When the bed depth is increased, the number of sorption sites is also increased. Thus, a large bed depth will take a larger time to become saturated with a similar amount of pollutant at a constant flow rate. The BDST equation parameters for Ni^{+2} in the (Zn-Ni) binary system, showed that the adsorptive capacity (N_o) for Ni^{+2} in (Zn-Ni) binary system at flow rates of 20 and 40 ml/min. are 0.46 and 0.50 mg/cm^3, respectively. So, there is slight effect of different flow rates on adsorption capacity. However, the data showed that the adsorptive capacity (N_o) for Ni^{+2} in (Cd-Ni) binary system at flow rates of 20 and 40 ml/min. are 1.47 and 0.68 mg/cm^3, respectively, i.e. the increasing in flow rate reduces the volume of nickel effluent treated at the breakpoint. This is due to the value of critical bed depth Z (cm) at flow rate of 40 ml/min. is twice than that of its value at flow rate of 20 ml/min.

Part (C): It includes the separation and recovery of zinc and cadmium ions in the two modes of operation (batch and column). The complete separation in batch mode, occurs by three successive cycles using virgin sorbent (RS-5) and with the suitable selected sorption medium molarity. Finally, the comparative cost of two processes (solvent extraction and adsorption) which may be used in the recovery of enriched materials (Zn^{-2} and Cd^{+2}) reveals that the adsorption onto noval sorbents are considered as a better replacement technology of solvent extraction, due to: (i) easy to handle, (ii) low cost and (iv) save foreign currancy.

Appendix(I)

Table(20) Surface mass transfer coefficients of Zn^{+2}, Cd^{+2} and Ni^{+2}.

Metal type	Sorbent type	Sorption medium molarity	$\ln(\frac{C'}{C'_o} - \frac{1}{1+mq_m})$	Time (min.)	C_e (mg/l)	C_e (mmol/l)	C_e/C_o	$\frac{1}{1+mq_m}$	$(\frac{C'}{C'_o} - \frac{1}{1+mq_m})$	β_i (cm min^{-1})
Zn^{+2}	RS-5	$0.01MNH_4Cl$	-0.9576	60	966.78	14.6853	0.96678	0.58300	0.38378	0.04651
			-1.0199	120	943.63	14.3336	0.94363		0.36063	
			-1.0653	180	927.61	14.0903	0.92761		0.34461	
			-1.1136	240	911.36	13.8435	0.91136		0.32836	
			-1.1793	360	890.48	13.5263	0.89048		0.30748	
		$0.10\ M\ NH_4Cl$	-1.0013	60	950.49	14.4379	0.9504		0.3674	0.05363
			-1.0642	120	928.00	14.0962	0.928		0.345	
			-1.1257	180	907.42	13.7836	0.9074		0.3244	
			-1.1731	240	892.45	13.5562	0.8924		0.3094	
			-1.2486	360	869.93	13.2141	0.8699		0.2869	
		$1.00\ M\ NH_4Cl$	-1.0483	60	933.55	14.1805	0.9335		0.3505	0.06368
			-1.1647	120	895.08	13.5962	0.8950		0.312	
			-1.2337	180	874.20	13.2790	0.8742		0.2912	
			-1.2873	240	859.09	13.0495	0.8590		0.276	
			-1.3582	360	840.18	12.7622	0.8401		0.2571	

Metal type	Sorbent type	Sorption medium molarity	$\ln(\frac{C}{C_o} - \frac{1}{1+mq_m})$	Time (min.)	C_e (mg/l)	C_e (mmol/l)	C_e/C_o	$\frac{1}{1+mq_m}$	$(\frac{C}{C_o} - \frac{1}{1+mq_m})$	β_i (cm min^{-1})
Zn^{+2}	RS-5	0.01 M HCl	-1.1950	60	885.75		0.8857		0.3027	6.422×10^{-6}
			-1.3509	120	842.00		0.842		0.259	
			-1.4354	180	821.00		0.821		0.238	
			-1.4929	240	807.76		0.8077		0.2247	
			-1.5297	360	799.60		0.7996		0.2166	
		0.10 M HCl	-1.1341	60	904.70		0.9047		0.3217	6.422×10^{-6}
			-1.2898	120	858.34		0.8583		0.2753	
			-1.3983	180	830.00		0.83		0.247	
			-1.4464	240	818.44		0.8184		0.2354	
			-1.4907	360	808.25		0.8082		0.2252	
		1.00 M HCl	-1.0598	60	929.58		0.9295		0.3465	6.422×10^{-6}
			-1.2204	120	878.19		0.8781		0.2951	
			-1.3104	180	852.76		0.8527		0.2697	
			-1.3819	240	834.14		0.8341		0.2511	
			-1.4242	360	823.70		0.8237		0.2407	
		5.00 M HCl	-1.0177	60	944.40		0.9444		0.3614	6.422×10^{-6}
			-1.1482	120	900.21		0.9002		0.3172	
			-1.2378	180	873.09		0.8730		0.29	
			-1.3060	240	853.99		0.8539		0.2709	
			-1.3676	360	837.74		0.8377		0.2547	

Metal type	Sorbent type	Sorption medium molarity	$\ln(\frac{C'}{C'_o} - \frac{1}{1+mq_m})$	Time (min.)	C_e (mg/l)	C_e (mmol/l)	C_e/C_o	$\frac{1}{1+mq_m}$	$(\frac{C'}{C'_o} - \frac{1}{1+mq_m})$	β_i (cm min^{-1})
Zn^{+2}	RP-5	0.01 M HCl	-1.0100	60	947.25	14.3886	0.9472		0.3642	0.392×10^{-6}
			-1.1162	120	910.54	13.8310	0.9105		0.3275	
			-1.2255	180	876.69	13.3168	0.8766		0.2936	
			-1.3220	240	849.64	12.9059	0.8496		0.2666	
			-1.4605	360	815.11	12.3814	0.8151		0.2321	
		0.10 HCl	-0.9514	60	969.27	14.7231	0.9692		0.3862	0.392×10^{-6}
			-1.0311	120	939.66	14.2733	0.9396		0.3566	
			-1.1325	180	905.21	13.7500	0.9052		0.3222	
			-1.2368	240	873.39	13.2667	0.8733		0.2903	
			-1.3614	360	839.31	12.7490	0.8393		0.2563	
		1.00 M HCl	-0.9195	60	981.78	14.9131	0.9817		0.3987	0.392×10^{-6}
			-0.9615	120	965.38	14.6640	0.9653		0.3823	
			-1.0723	180	925.21	14.0538	0.9252		0.3422	
			-1.1679	240	894.06	13.5807	0.8940		0.311	
			-1.1946	360	885.83	13.4557	0.8858		0.3028	

Metal type	Sorbent type	Sorption medium molarity	$\ln(\frac{C}{C_o} - \frac{1}{1+mq_m})$	Time (min.)	C_e (mg/l)	C_e (mmol/l)	C_e/C_o	$\frac{1}{1+mq_m}$	$(\frac{C}{C_o} - \frac{1}{1+mq_m})$	β_i (cm min^{-1})
Zn^{+2}	RP-I	0.01 M HCl	-0.9819	60	957.62	14.5462	0.9576		0.3746	0.18921
			-1.0659	120	927.41	14.0873	0.9274		0.3444	
			-1.1132	180	911.55	13.8464	0.9115		0.3285	
			-1.1294	240	906.25	13.7658	0.9062		0.3232	
			-1.1447	360	901.36	13.6916	0.9013		0.3183	
		0.10 M HCl	-0.9233	60	980.28	14.8904	0.9802		0.3972	0.21266
			-1.0174	120	944.56	14.3478	0.9445		0.3615	
			-1.0587	180	929.90	14.1251	0.9299		0.3469	
			-1.0900	240	919.26	13.9635	0.9192		0.3362	
			-1.1020	360	915.23	13.9023	0.9152		0.3322	
		1.00 M HCl	-0.9023	60	988.67	15.0178	0.9886		0.4056	0.2004
			-0.9309	120	977.22	14.8439	0.9772		0.3942	
			-0.9800	180	958.39	14.5579	0.9583		0.3753	
			-1.0155	240	945.22	14.3578	0.9452		0.3622	
			-1.0535	360	931.72	14.1527	0.9317		0.3487	

Metal type	Sorbent type	Sorption medium molarity	$\ln(\frac{C}{C_o} - \frac{1}{1+mq_m})$	Time (min.)	C_e (mg/l)	C_e (mmol/l)	C_e/C_o	$\frac{1}{1+mq_m}$	$(\frac{C}{C_o} - \frac{1}{1+mq_m})$	β_i (cm min^{-1})
Cd^{+2}	RS-5	0.01 M NH_4Cl	-2.6104	60	949.60	8.07716	0.9496	0.87610	0.0735	#NUM!
			-4.1669	120	891.66	7.58433	0.8916		0.0155	
			#NUM!	180	844.22	7.18081	0.8442		-0.0319	
			#NUM!	240	812.54	6.91135	0.8125		-0.0636	
			#NUM!	360	807.82	6.87120	0.8078		-0.0683	
		0.10 M NH_4Cl	-3.4737	60	907.15	7.71609	0.9071		0.031	#NUM!
			#NUM!	120	854.56	7.26876	0.8545		-0.0216	
			#NUM!	180	822.22	6.99368	0.8222		-0.0539	
			#NUM!	240	797.76	6.78563	0.7977		-0.0784	
			#NUM!	360	793.02	6.74531	0.7930		-0.0831	
		1.00M NH_4Cl	-5.0359	60	882.63	7.50752	0.8826		0.0065	#NUM!
			#NUM!	120	820.58	6.97973	0.8205		-0.0556	
			#NUM!	180	784.79	6.67531	0.7847		-0.0914	
			#NUM!	240	772.48	6.57060	0.7724		-0.1037	
			#NUM!	360	770.84	6.55665	0.7708		-0.1053	

Metal type	Sorbent type	Sorption medium molarity	$\ln(\frac{C}{C_o} - \frac{1}{1+mq_m})$	Time (min.)	C_e (mg/l)	C_e (mmol/l)	C_e/C_o	$\frac{1}{1+mq_m}$	$(\frac{C}{C_o} - \frac{1}{1+mq_m})$	β_i (cm min^{-1})
Cd^{+2}	RS-5	0.01 M HCl	-2.5269	60	956.04	8.13194	0.9560		0.0799	1.9079×10^{-6}
			-2.7838	120	937.91	7.97773	0.9379		0.0618	
			-2.9759	180	927.12	7.88595	0.9271		0.051	
			-3.0470	240	923.61	7.85609	0.9236		0.0475	
			-3.0512	360	923.40	7.85431	0.9234		0.0473	
		0.10 M HCl	-2.7150	60	942.35	8.01549	0.9423		0.0662	1.9079×10^{-6}
			-3.0554	120	923.23	7.85286	0.9232		0.0471	
			-3.1893	180	917.34	7.80276	0.9173		0.0412	
			-3.2834	240	913.60	7.77095	0.9136		0.0375	
			-3.2914	360	913.39	7.76916	0.9133		0.0372	
		1.00 M HCl	-2.9977	60	926.06	7.87693	0.9260		0.0499	3.8158×10^{-6}
			-3.5065	120	906.10	7.70716	0.9061		0.03	
			-3.7679	180	899.21	7.64855	0.8992		0.0231	
			-3.8121	240	898.21	7.64004	0.8982		0.0221	
			-3.9792	360	894.86	7.61155	0.8948		0.0187	
		5 M HCl	-3.2781	60	913.89	7.77342	0.9138		0.0377	7.6316×10^{-6}
			-4.1351	120	892.16	7.58858	0.8921		0.016	
			-4.5282	180	886.92	7.54401	0.8869		0.0108	
			-4.7217	240	885.07	7.52828	0.8850		0.0089	
			-5.0206	360	882.73	7.50837	0.8827		0.0066	

Metal type	Sorbent type	Sorption medium molarity	$\ln(\frac{C}{C_o} - \frac{1}{1+mq_m})$	Time (min.)	C_e (mg/l)	C_e (mmol/l)	C_e/C_o	$\frac{1}{1+mq_m}$	$(\frac{C}{C_o} - \frac{1}{1+mq_m})$	β_i (cm min^{-1})
Cd^{+2}	RP-5	0.01M	-2.418	60	965.25	8.21028	0.9652		0.0891	0.5829×10^{-6}
		HCl	-2.8018	120	936.85	7.96871	0.9368		0.0607	
			-3.3298	180	911.93	7.75674	0.9119		0.0358	
			-3.6496	240	902.11	7.67322	0.9021		0.026	
			-3.9580	360	895.24	7.61478	0.8952		0.0191	
										0.46632×10^{-6}
			-2.2995	60	976.43	8.30537	0.9764		0.1003	
		0.10 M HCl	-2.5678	120	952.84	8.10472	0.9528		0.0767	
			-2.9393	180	929.07	7.90254	0.9290		0.0529	
			-3.1677	240	918.22	7.81021	0.9182		0.0421	
			-3.4609	360	907.50	7.71906	0.90750		0.0314	0.46632×10^{-6}
						8.40004	0.9875		0.11146	
			-2.1940	60	987.56	8.21419	0.9657		0.08961	
		1.00 M HCl	-2.4122	120	965.71	8.03429	0.9445		0.06846	
			-2.6814	180	944.56	7.92193	0.9313		0.05525	
			-2.8957	240	931.35	7.85056	0.9229		0.04686	
			-3.0604	360	922.96					