Chapter 6

Application of the adsorbents to some Real and Synthetic Samples

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6.1. Introduction.

In the environment, contamination rarely occurs for single metals and is invariably due to complex mixtures. Nonetheless, routine evaluation of adsorbates is made based on single adsorbate components. Competitive adsorption on the adsorbent surface can take place where components with similar properties (i.e., size, polarity, interaction energy) compete for a limited number of adsorption sites.

Nuclear technology has resulted in release of radioactive isotopes of cesium into environment. ^{137}Cs is one of the most abundant radionuclides in the nuclear fission having long radiological half-life (30 years) and can be present along with uranium [1-3]. Its metabolic similarities to potassium favour its uptake and accumulation by plants after radio-contamination of water body and ultimately agricultural field. It enters into many food chain pathways to cause radiation exposure to human being and other ecological biota of the ecosystem [4]. Futhermore Fe^{3+} is known to be present in mining feed solution and also is a major constituent in high and low level nuclear industry effluents [5, 6].

Thus, a better understanding of the multi-component adsorption from aqueous solutions is needed.

The removal of heavy metals from industrial wastewaters is gaining significance in the present context of global ecology. Chromic acid is used in the plating and anodizing operations in the surface finishing industry. Chromate eventually finds its way to a company's waste treatment system through the dumping of the spent plating baths, contaminated rinse waters, and fume scrubber blow down. Both the spent plating bath and contaminated rinse waters are acidic; however, they generally differ in the amount of chromate contained. The former is apparently very concentrated (ranging from 45 to 470 g of Cr^{6+}/L), while the latter can be relatively dilute and can be further classified as high strength, typical strength, or dilute wastewaters with typical Cr^{6+} levels of 500, 100, and 20 ppm, respectively [7].

So our objectives were:

i) To investigate the adsorption ability of the adsorbents under study (PSP, APSP, SAPSP, PAPSP, 9AAC and MPSP) for Cu, Cd, Zn and Hg in binary, ternary and quaternary metal solution mixtures

ii) To study the effect of the presence of Fe^{3+} and Cs^{+} on the adsorption of uranium using the adsorbents under study

iii) To study the application of the adsorbents under study for the removal of chromium from chrome plating effluents

6.2. Materials and Methods.

6.2.1. Batch Uptake.

Adsorption experiments were performed in batch mode for Cu^{2+}, Cd^{2+}, Zn^{2+} and Hg^{2+} (from stock solutions as described in Chapter 3) conducted at 30°C by agitating 0.1 g of adsorbent with respective metal ion solution in 100mL stoppered conical flasks in a thermostated rotary mechanical shaker at 150 rpm for 4 hours.

6.2.1.1. ***Synthetic Mixtures.*** Binary mixtures contained 25 ppm of each metal ion, ternary mixtures contained 11 ppm of each metal ion and quaternary mixtures contained 6.25 ppm of each metal ion. Batch experiments were performed by taking 20 mL of adsorbate solution containing different mixtures of metal ions under study maintained at pH 4 and 0.1 g of adsorbent in 25 mL stoppered flasks. The contents were shaken by a thermostated water bath shaker with a constant speed of 150 rpm at 30°C and the samples were withdrawn at appropriate time intervals and filtered. The filtrate was analyzed for each of the metals Cu, Cd, Zn and Hg by AAS at their respective wavelengths.

6.2.1.2. ***Selectivity Coefficient.*** The effectiveness of the removal of each metal ion is reflected in the percentage adsorption and selectivity coefficient as reported in Figures 6.1, 6.2, 6.3 and Table 6.1 respectively. The selectivity coefficient k was calculated using the equation [8, 9]:

$$k = \frac{molar\ fraction\ of\ component\ i\ in\ the\ carbon\ adsorbed\ mixture}{molar\ fraction\ of\ component\ i\ in\ the\ aqueous\ solution\ mixture} = \frac{q_i/(q_i+q_j)}{C_{Li}/\ (CL_i+CL_j)}$$

6.3. Results and Discussion.

6.3.1. Synthetic Mixtures

6.3.1.1. ***Effect of competitive heavy metals in binary, ternary and quaternary system (Cu, Cd, Zn and Hg).*** In quaternary mixtures PAPSP, APSP, SAPSP, 9AAC and MPSP showed higher selectivity towards zinc while PSP showed greater preference towards mercury followed by zinc. SAPSP and PAPSP showed their next preference to copper followed by mercury while APSP, 9AAC and MPSP showed their next preference to mercury over copper.

In ternary mixtures containing Cu, Cd and Hg where zinc was absent all the adsorbents under study showed higher selectivity towards mercury except for SAPSP which showed preference to copper over mercury as also seen in quaternary mixtures. Even in solutions containing Hg, Zn and Cu PSP, MPSP and APSP showed selectivity towards mercury. However, PAPSP and 9AAC again showed better selectivity towards zinc followed by mercury. SAPSP showed selectivity towards copper followed by mercury and zinc. Between copper and cadmium no specific trend was observed with some adsorbents showing selectivity towards copper (PSP, APSP, MPSP) and some towards cadmium (PAPSP) after Hg and Zn.

In bimetallic mixtures of copper and mercury greater selectivity towards mercury was observed by PSP, PAPSP, 9AAC and MPSP. PAPSP showed five times higher selectivity for mercury over copper. On the other hand APSP and SAPSP showed better selectivity towards copper.

Adsorption studies on binary mixtures containing Cd and Hg revealed that all the adsorbents under study showed higher selectivity towards mercury as compared to Cd. Similar studies on binary mixtures containing Zn and Hg revealed that all the adsorbents were selective towards Zn over mercury. However MPSP had almost equal selectivity coefficient values for Zn and Hg.

In binary mixtures containing Cu and Cd, the selectivity coefficients were higher for Cu than Cd in the case of APSP, SAPSP, PAPSP and 9AAC while PSP and MPSP had greater selectivity coefficient values for Cd. APSP, SAPSP, PAPSP and 9AAC displayed higher selectivity towards copper in binary mixtures containing Cu and Zn while PSP and MPSP

showed greater selectivity towards zinc. On the other hand, in binary mixtures containing Cd and Zn, PSP, 9AAC, APSP and MPSP showed higher selectivity coefficient for Cd while SAPSP, PAPSP had higher selectivity coefficient for Zn.

In summary, SAPSP seems to show a clear preference for copper except in quaternary mixtures where Zn has a slightly higher selectivity coefficient, however the difference is very less. PSP on the other hand displayed a greater selectivity towards mercury except for binary mixtures. In binary mixtures probably where individual metal concentrations are higher though the total metal ion concentration continues to be the same PSP showed a different trend by displaying greater selectivity towards Cd in the presence of Cu and Zn, a greater selectivity towards mercury in the presence of Cd and Cu and a greater selectivity towards Zn in Hg-Zn mixtures. PAPSP showed a clear preference to Zn in quaternary and ternary mixtures and in Cd-Zn and Hg-Zn binary mixtures. Surprisingly, PAPSP showed six times higher selectivity coefficient for copper over Zn in their binary mixtures. MPSP seems to show a clear preference towards mercury in binary and ternary mixtures. However in quaternary mixtures it showed preference towards Zn. APSP and 9AAC did not show any specific trend in the present studies with its selectivity coefficients changing in quaternary, ternary and binary mixtures. This variation in specificity could be because the binding strength of a metal ion to a given adsorbent depends on various properties of the adsorbent and the adsorbate namely ionic radius, hydrolysis constant and electro-negativity of the adsorbate as well as the functional groups and porosity of the adsorbent. It also depends on multiple mechanisms involved in adsorption like ion exchange, chemisorptions, physic-sorption, dipole interactions, intra-particle diffusion, pore diffusion etc. However, it is observed that mercury and zinc showed quantitative adsorption (>90%) in binary, ternary and quaternary mixtures with most of the adsorbents under study. Thus further studies using different concentrations and adsorption models are definitely warranted to get a clear picture of the selectivity.

Table 6.1. Selectivity of binary, ternary and quaternary mixtures of Cu, Cd, Zn and Hg

	Binary Mixtures											
	Cu+Hg		Cd+Hg		Zn+Hg		Cu+Cd		Cu+Zn		Cd+Zn	
	Cu	Hg	Cd	Hg	Zn	Hg	Cu	Cd	Cu	Zn	Cd	Zn
PSP	0.720	1.508	0.748	1.452	1.054	0.948	0.721	1.457	0.993	1.006	1.377	0.755
APSP	1.297	0.808	0.607	2.368	2.816	0.559	1.106	0.910	1.647	0.681	1.118	0.901
SAPSP	1.125	0.898	0.710	1.621	1.672	0.706	1.372	0.774	1.958	0.635	0.777	1.388
PAPSP	0.576	2.978	0.652	2.055	1.019	0.981	1.490	0.734	3.378	0.535	0.669	1.925
9AAC	0.809	1.261	0.731	1.487	1.161	0.866	1.648	0.688	1.567	0.683	1.485	0.714
MPSP	0.878	1.143	0.719	1.540	0.965	1.036	0.743	1.401	0.944	1.060	1.535	0.701

	Ternary Mixtures											
	Cu+Cd+Zn			Cu+Cd+Hg			Hg+Zn+Cu			Hg+Zn+Cd		
	Cu	Cd	Zn	Cu	Cd	Hg	Hg	Zn	Cu	Hg	Zn	Cd
PSP	1.144	0.563	1.591	0.787	0.662	2.644	2.385	0.755	0.751	15.966	0.957	0.495
APSP	1.107	0.749	1.257	1.069	0.771	1.266	1.299	0.761	1.066	6.724	1.055	0.481
SAPSP	0.923	0.799	1.467	1.118	0.840	1.086	1.029	0.904	1.081	11.567	2.988	0.359
PAPSP	0.450	1.150	3.450	0.666	1.076	1.627	0.938	1.957	0.697	8.531	2.901	0.373
9AAC	0.808	0.842	1.482	0.799	0.725	1.938	0.889	12.807	0.492	1.590	12.857	0.366
MPSP	0.980	0.777	1.338	0.823	0.608	2.714	1.730	0.736	0.903	9.669	1.772	0.353

	Quaternary Mixtures			
	Cu+Cd+Zn+Hg			
	Cu	Cd	Zn	Hg
PSP	1.38E-02	2.95E-03	0.033	0.960
APSP	0.059	0.065	0.271	0.155
SAPSP	0.188	1.78E-02	0.203	0.133
PAPSP	0.124	0.063	0.227	0.055
9AAC	5.96E-03	1.91E-03	0.172	9.33E-03
MPSP	1.09E-02	2.75E-03	0.041	0.027

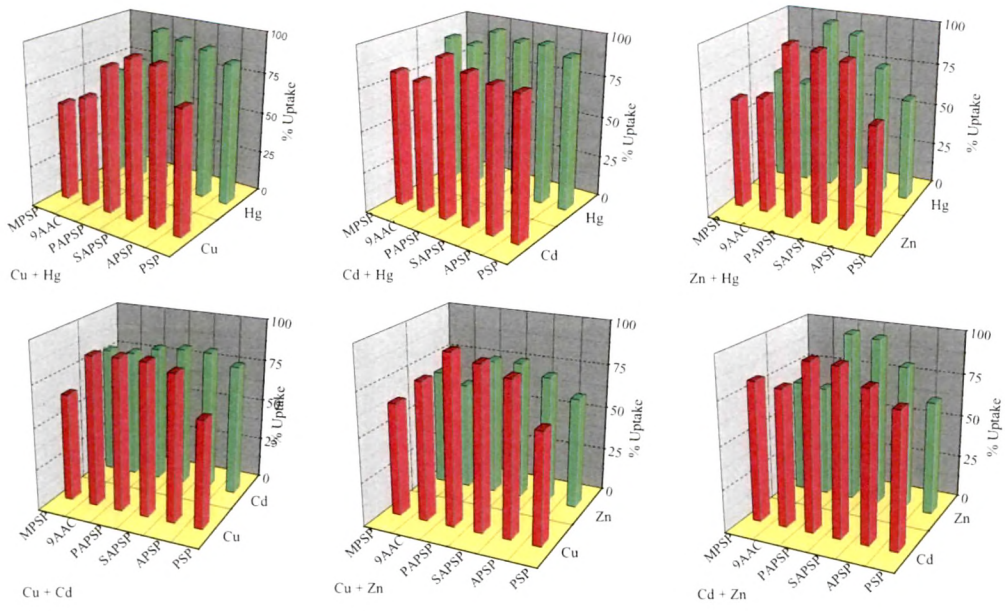

Figure 6.1. % Uptake for Binary Mixtures

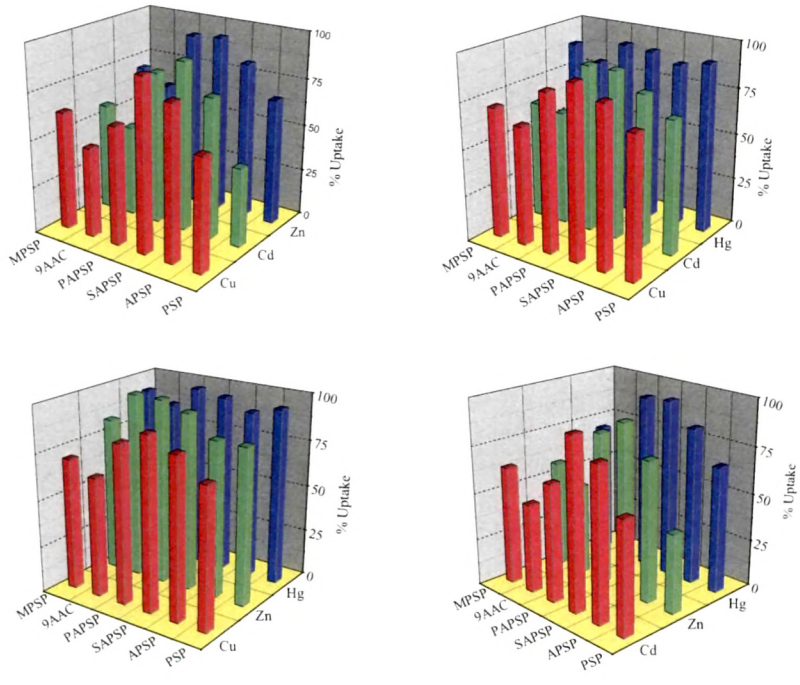

Figure 6.2. % Uptake for Ternary Mixtures

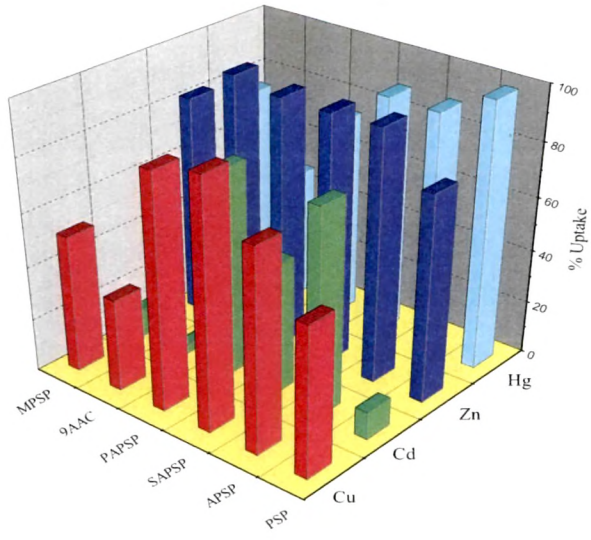

Figure 6.3. % Uptake for Quaternary Mixtures

6.3.1.2. ***Effect of Fe^{3+} and Cs^{+} on uptake of U^{6+}.*** The effect of co-ions like Fe^{3+} and Cs^{+} on the adsorption of U^{6+} by the adsorbents under study was tested in binary and ternary metal systems. About 0.1 g of each adsorbent under study was agitated with 25mL of binary or ternary metal solutions containing equimolar concentrations (1000 mg/L) of UO_2^{2+}, Cs^{+} and Fe^{3+} maintained at pH 1.0, at 30°C. After the established contact time (4 h) was attained, the suspension was filtered, and filterate was analyzed for the metal concentration. The adsorption processes are represented by the distribution coefficient K_d where K denotes the distribution of the ion of interest between the solid phase and the aqueous phase [10].

The obtained results as adsorbed amount of each cation are summarized in Table 6.2. It is evident from the table that the presence of Cs^{+} and Fe^{3+} cations, in binary systems and ternary systems did not cause any interference in the uptake of U^{6+} and the uptake of all the three ions was quantitative at high concentrations of all the three ions when present simultaneously (1000 ppm each). Similar observations were made by Sudhir et al [11].

Table 6.2. Selectivity of Uranium over iron and cesium

% Extraction						
U+Fe						
	PSP	APSP	SAPSP	PAPSP	9AAC	MPSP
Fe	97.02	98.82	98.26	98.96	98.56	96.14
U	97.98	98.8	98.54	99.36	98.62	96.86
U+Cs						
Cs	98.16	99.18	98.74	99.26	98.82	96.48
U	96.86	98.16	98.38	98.54	97.58	97.02
U+Cs+Fe						
Cs	97.56	97.98	97.7	99.02	98.02	96.06
Fe	96.14	97.38	97.14	98.44	97.54	95.18
U	96.38	98.06	97.74	99.06	98.3	95.62
K_d						
U+Fe						
Fe	6.611	16.849	11.394	19.131	13.789	5.081
U	9.801	16.566	13.598	31.150	14.393	6.269
U+Cs						
Cs	10.769	24.290	15.773	26.927	16.849	5.582
U	6.269	10.769	12.245	13.598	8.164	6.611
U+Cs+Fe						
Cs	8.096	9.801	8.595	20.308	10.001	4.976
Fe	5.081	7.533	6.893	12.720	8.030	4.049
U	5.425	10.209	8.749	21.176	11.664	4.466
Selectivity Coefficient						
U+Fe						
Fe	1.482	0.983	1.193	1.628	1.044	1.234
U+Cs						
Cs	0.582	0.443	0.776	0.505	0.485	1.184
U+Cs+Fe						
Cs	0.670	1.042	1.018	1.043	1.166	0.898
Fe	1.067	1.355	1.269	1.665	1.453	1.103

6.3.2. Application to Real Effluent

6.3.2.1. ***Chrome Plating Effluent.*** The adsorbents under study were tested for their efficacy to remove chromium from chromium plating waste water collected from a chrome plating industry of GIDC, Ankleshwar, India. Exact concentrations of the metals of interest were measured by ICP analysis. The waste water was acidified using 1M HNO_3 to dissolve the precipitates, and pH of the solution found to be pH 1. Solution was analysed using ICP analysis for finding out the presence of metal ions and their concentration. Further the acidified chrome plating effluent was treated with adsorbents under study. A series of flasks containing 25 mL acidified effluent, along with 100mg adsorbents under study were placed for shaking in a thermostated rotary mechanical shaker for 180 mins. The amount of metal remaining in the solution was determined by ICP analysis.

Table 6.3. Composition of the chrome plating effluent sample

Metal ions	Conc. (ppm)	Metal ions	Conc. (ppm)	Metal ions	Conc. (ppm)
Al	13.0	Ni	10.7	Zn	76.0
K	19.9	Cr	51.8	Ca	214
Mg	35.9	Pb	3.35	Na	480
Cu	7.57	Fe	136.0	Cd	0.5
Hg	0.14	V	0.11	As	0.09

A detailed composition of the plating effluent sample collected from chrome plating industry in GIDC, Ankleshwar, India is presented in Table 6.3. The chromium concentration in the effluent is 51.8 ppm. The results of the experiments with the percent extraction, K_d value and selectivity coefficient are shown in table 6.4. It is seen that SAPSP is the most effective adsorbent capable of removing more than 90% of Fe, Ni, Cd and Cr, more than 80% of Zn, V and As, 78% of Hg and 64% of Pb. PSP, APSP and SAPSP were able to remove Cr quantitatively from plating effluent. Selectivity coefficient was found to be highest for Cr over other metals (103 times over Fe, Ni, Pb and Hg) present in the effluent for APSP.

6.3.2.2. ***Environmental relevance.*** Because chrome-plating rinsewaters are acidic, it is an advantage that the maximum uptake for chromate by biosorbents is obtainable at pH 1. Adjustment of the rinse-water pH will thus only require less volume of mineral acid/base solution. The disadvantage lies in the fact that biosorbent-bound chromate cannot be recovered completely as chromate but also as Cr(III). However, unlike other adsorbents reported in literature wherein the reduced Cr(III) is observed in solution , in the present study the reduced Cr(III) remained adsorbed onto the adsorbents under study. Although only tested in laboratory scale, the removal of chromium from plating waste water using palm shell based adsorbents appears to be a promising approach APSP seems to be the most promising adsorbent because of its high chromium selectivity coefficients with respect to Zn, Pb, Hg, Ni and Fe. Thus there is excellent potential to remove toxic heavy metals from the plating effluent using these adsorbents under study, providing a viable and cost-effective technology for waste water treatment.

Table 6.4. Selectivity of Chromium over other inorganic ions present in chrome plating effluent

% Extraction						
	PSP	APSP	SAPSP	PAPSP	9AAC	MPSP
Zn	17.11	11.84	85.92	22.63	16.45	15.79
Cd	40.00	98.00	98.00	98.00	40.00	50.00
Pb	40.29	37.31	64.18	55.22	49.25	40.29
Hg	78.57	21.43	78.57	85.71	92.86	92.86
V	63.64	90.91	81.82	86.36	90.91	90.91
As	33.33	88.89	88.89	88.89	44.44	66.67
Cu	85.47	99.87	32.63	28.67	2.25	6.21
Ni	91.59	21.49	95.33	45.79	33.64	41.12
Fe	23.38	27.94	93.46	47.79	27.94	31.62
Cr	95.95	99.83	94.98	53.67	44.02	42.08
Distribution ratio K_d						
	PSP	APSP	SAPSP	PAPSP	9AAC	MPSP
Zn	0.052	0.034	1.526	0.073	0.049	0.046
Cd	0.167	12.250	12.250	12.250	0.167	0.250
Pb	0.169	0.149	0.448	0.308	0.243	0.168
Hg	0.917	0.068	0.917	1.500	3.250	3.250
V	0.438	2.500	1.125	1.583	2.500	2.500
As	0.125	2.000	2.000	2.000	0.200	0.500
Cu	1.470	189.000	0.121	0.100	0.006	0.016
Ni	2.722	0.068	5.100	0.211	0.127	0.174
Fe	0.076	0.097	3.570	0.229	0.097	0.115
Cr	5.917	143.639	4.731	0.289	0.197	0.181
Selectivity Coefficient						
	PSP	APSP	SAPSP	PAPSP	9AAC	MPSP
Zn	114.756	4277.280	3.101	3.960	3.994	3.882
Cd	35.520	11.725	0.386	0.023	1.179	0.728
Pb	35.081	965.260	10.562	0.939	0.810	1.078
Hg	6.4581	2106.720	5.161	0.193	0.060	0.056
V	13.531	57.456	4.205	0.182	0.078	0.072
As	47.360	71.820	2.365	0.144	0.983	0.364
Cu	4.025	0.760	39.073	2.882	34.231	10.997
Ni	2.174	2098.393	0.927	1.371	1.550	1.042
Fe	77.592	1481.760	1.325	1.265	2.028	1.574

6.4. Conclusions.

Competetive adsorption in case of binary ternary and quaternary mixtures of Cu, Cd, Zn and Hg was found in agreement with the adsorption of particular metal ions in Chapter 3 but no particular trend is been observed. Further in case of uranium adsorbents showed better affinity towards uranium in presence of its competitive inorganic ions (Fe and Cs). Adsorbents were found to have satisfying selectivity coefficients for chromium over other adsorbates in chrome plating effluent.

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