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Development and optimization of magnetic technologies based processes for removal of some toxic heavy metals

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Abstract In the developing countries where the cost is often a decisive factor, extensive studies were undertaken to test the most effective factors on the preparation, optimization and validation of the magnetic particles (or, more accurately, magnetizable particles) for removal of heavy metals from wastewaters. The objective of the proposed work was focused to provide promising solid-phase materials, which, are relatively in expensive and combine high surface capacity with fast efficient treatment. Four various metal oxides including hydrous ferric oxide (HFO), hydrous stannic oxide (HSO) and mixed ferric/stannic oxide (HMO), were prepared by precipitation with ammonia from metal chloride solutions. Two mixed oxides were prepared with different Sn/Fe ratios of 50% and 20%. Optimal conditions for the activation of these particles and the subsequent mixing of various metals oxides are tested together with the utility of the method to get a new composite material with developed chemical characteristics over their individual metal oxides. Factors affecting the sorption behavior of the prepared samples in basic and acid media were elucidated. The magnetic treatment procedure using the mixed oxide (50%) enables the equilibration step to be carried out rapidly mainly due to ferric oxide during the magnetization process and efficiently due to high capacity of the stannic oxide. A key factor in achieving very high uptake percentage is the reduction of non-specific binding of various heavy metals to the solid phase support. This is usually achieved by increasing the ion exchange capability, in addition to their adsorption process.

Keywords Heavy metals · Magnetic technology · Composite oxide

1 Introduction

Looking for solid phase magnetic technology-based processes for heavy metals removal and separation in conventional scientific literature, simple examples are found. This reflects the fact that magnetic technologies have not yet found wide applications in spite of their advantages. The few established fields include the removal of corrosion products from the condensate circuit of power plants and in particular of nuclear power plants (Rodgers et al. 1981); the separation of the finest metal particles from the wastewaters of steel and iron industries (Harland et al. 1976). In addition, a number of applications have been implemented on the technical scale, although they have not yet been generally accepted on the market.

Most of the basic concepts underlying these processes were developed in 1970s and 1980s. However, industrial exploitation was prevented by the high costs of the magnetic systems available at that time. But, costs of superconducting magnetic coils and, in particular, of permanent magnet systems based on heavy metals and rare earths (e.g. cadmium, titanium, neodymium or samarium) dropped considerably during the past decade, such that it is now considered worthwhile to again investigate and evaluate these approaches in a modified form, considering modern magnetic technology. In addition to this relatively small number of technically implemented applications, several methods have already been tested on the laboratory or pilot scale such as magnetic methods for material separation (Tamaura et al. 1991; Svoboda and Fujita 2003). Based on magnetic technology, innovative approaches have been conceived to solve some

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difficulties regarding heavy metals pollution (Hu et al. 2005; Xuan et al. 2007).

It is well known that magnetism plays an important role as separating tool in the mineral processing industry. In recent years, different types of magnets with fields ranging from 0.05–2 Tesla have been used to separate ferromagnetic materials from diverse kinds of mineral ores. The creation of high magnetic field gradient is of highly importance in these magnetic separation processes (Watson 1991; Terashima et al. 1986).

The magnetic particles used as heavy metals sorbents must fulfill the following criteria, the size and density of the particles should be low enough to prevent spontaneous sedimentation during pre-equilibration step, the particles should have high capacity for heavy metals uptake and they should have a high magnetic susceptibility to facilitate rapid sedimentation in a magnetic field of moderate intensity (Watson 1994; Ito et al. 1985).

Iron oxides in various forms have been used for treatment of radioactive and heavy metals from water and wastewater solutions (Misak et al. 1996; Ghoniemy et al. 1999, 1997; Morcos et al. 2003). For example iron ferrite supported and used in a column mode in the presence of an external magnetic field has an enhanced capacity removal of contaminants in various forms from water. The magnetic field enhanced filtration/sorption process shows promising prospect as an improved, simple and inexpensive method of removal of contaminants in groundwater and other water sources. Stannic oxide is extensively used in chemical separations (Sharp et al. 1998; Ruvarac 1998). Mixed oxides have been only very little studied and a study of mixed Fe (III)/Sn (IV) oxide would be of particular interest.

At present, composite exchanger materials are the state of the art materials in many applications and column operation. They are by far the most suitable exchangers for environmental treatment of hazardous radioactive and industrial waste. Thus the present work is oriented to develop a new and inexpensive magnetic filtration/sorption technology for applying in different fields such as removal of heavy toxic metals and purifying of the hazardous waste waters. The process is based on the use of supported surface complex adsorbent such as iron oxide mixed with stannic oxide to form a new homogeneous surface mixed oxide. Thus, the main contribution of this work is regards to the combination of the theoretical aspects of magnetizable particles with their possible application in ecotechnologies.

1.1 Physical fundamental s of magnetic process

All type of magnetic separators is based on the property of magnetic field exerting a force on matter. The general relationship for this magnetic force F_m is as follows.

$$F_m = \mu_o V_p M_p \operatorname{grad} H$$

where μ_o denotes the permeability constant of the vacuum, V_p the particle volume, M_p particle magnetization and $\operatorname{grad} H$ is the gradient magnetic field strength at the position of the particle. Particle magnetization may be expressed by the magnetic volume susceptibility χ and magnetic field strength H as follows:

$$M_p = \chi H$$

where the volume susceptibility is a constant for diamagnetic and paramagnetic substances and a function among others of the particle shape and size as well as the field strength for ferromagnetic and ferrimagnetic substances.

As the type of particles to be treated is usually given, the magnetic force achievable in a separator can be influenced by the prevailing field strength. Simple plate-type separators reach comparatively moderate values for these parameters.

2 Experimental

2.1 Reagents and solutions

All chemicals used in this work of analytical grade of E.Merck or BDH. Aqueous solutions were prepared with double distilled de-ionized water. Standard stock solutions (1000-ppm) of Pb (II) and Cd (II) were prepared by dissolving requisite amounts of their salts, in 5.0-ml of hydrochloric acid (39%) and moderate heating was applied. Each solution was quantitatively dissolved in double distilled de-ionized water containing 5% of nitric acid. Mixed working standards containing different concentrations proportional to the respective detection limits were prepared by the dilution of the stock solutions for calibrations.

2.2 Preparation of solid phase magnetizable particles by chemical precipitation

In our laboratories there are three compatible areas to achieve our goals. The first area is focusing on the optimum preparation method of magnetizable particles. The second area is dealing with identification and characterization of the prepared magnetic particles. The third area is mainly focusing on application and validation of magnetic technologies for heavy metal removal from surface wastewater. Hydrous ferric oxide, stannic oxide and mixed ferric/stannic oxide will be designated as HFO, HSO and HMO, respectively, throughout this work.

2.3 HFO

There are two methods for the preparation of magnetic iron oxide starting from the crystals of anhydrous iron compounds.

Iron ferrite can be easily prepared from a solution containing ferric and ferrous ions with a ratio of Fe (III)/Fe (II) equal 2. In this respect, iron ferrite solids are crystalline materials, unlike hydroscopic metals hydroxide sludge's and can be more readily filtered. In addition their ferromagnetic character permits subsequently use of magnetic separation of liquid phase containing heavy metals from the solids particles by means of magnetic separators.

Also, magnetite (FeO Fe_2O_3) samples is prepared by precipitation of iron (II) ions by the addition of sodium hydroxide solution in the form of Fe $(OH)_2$, followed by oxidation of the precipitate with oxygen. The formed magnetite is an iron (II)/iron (III) mixed oxide having the solid structure of an inverse spinal. In the absence of an external magnetic field, activated magnetite readily adsorbs numerous heavy metal species.

To gather the advantages of ferrite and magnetite, a stoichiometric amount of 0.25 M NH_4OH was added to 0.25 M $FeCl_3$ (Ghoniemy et al. 1997). After settling over-night, the solid product was repeatedly washed with water by decantation over one day. It was then filtered under suction, dried at 50 °C and allowed to breakdown in hot water. After being filtered, it was abundantly washed (∼2 weeks) with a dilute (∼10%) solution of ammonia until the washings were free of Cl^- ions. This was followed by washing (∼3 weeks) with distilled water until the washings had a pH of about 6. Subsequently, the solid was filtered, dried at 50 °C, sieved to different sizes and stored over saturated NH_4Cl. With all the hydrous oxides prepared, washing was always carried out by contacting, with intermittent shaking, the solid with the washing solution (or water) in a large container. The washing solution was renewed twice daily.

2.4 HSO

Besides, another sample (hydrous oxides of Sn (IV)) was prepared by precipitation of homogeneous solution of 0.25 M $SnCl_4$ as previously done. This sample was used for comparison with iron-containing materials and was investigated with respect to developing magnetic absorbability.

2.5 Mixed composite (HMO)

To prevent later re-dissolution, the ferrite sludge is often subjected to a thermal treatment at 200–400 °C. As known from pure magnetite formation, synthesis from iron (II) and iron (III) hydroixide mixtures exhibits much smaller temperature dependence than synthesis via oxidation of iron (II) hydroxide. This is why the so-called "mixing method". In the course of this thermal treatment, even those heavy metal ions that are initially bound by ion exchange only are incorporated into the crystal lattice.

Satisfactory saturation magnetizations were reached by the so-called "mixing method". A composite consisting of stannic compound and magnetite particles were prepared. Thus two different samples of materials containing iron were prepared as a source of magnetizable particles. Various molar ratio of Sn/Fe were prepared to gives the composition ratios 50 and 20%. Mixing method of tin-containing materials Sn/Fe shows satisfactory magnetic properties of the reaction products even at a room temperature of 25 °C down to a Sn/Fe molar ratio of about 20%.

Ferric oxide is a principal factor. Due to its magnetic properties, the composite particles can be separated efficiently by the plate magnetic separator even with high filtration rates. Besides, samples of the iron-containing metals will be prepared for improvement the magnetic susceptibility. Hydrous oxides of mixed Fe (III)–Sn (IV) were prepared by precipitation from homogeneous mixed solutions.

2.6 Physical characteristics of the prepared magnetic materials

Some physical characteristics of the prepared magnetic materials were previously tested in part-1 (Ghoniemy et al. 1999). Analysis (X-ray, infra-red, thermal) had shown that HFO and HMO are amorphous, whereas HSO is microcrystalline. It also showed that all the samples are oxides containing adsorbed H_2O molecules and surface OH groups. In addition, it revealed that HMO is not a simple mixture of HFO and HSO.

The TGA curves and DTA analysis (not given here for brevity) showed a continuous loss in weight up to the maximum heating temperature used (500 °C). The ignition losses of HFO, HSO and HMO were found to be 25.7%, 17.0% and 21.9%, respectively, which gives the empirical formulae $Fe_2O_3.3.07\ H_2O$, $SnO_2.1.71\ H_2O$ and $SnO_2.3.58\ H_2O$ (Ghoniemy et al. 1999). At 200 °C, the water remaining in the oxides corresponds to 5.9%, 7.3% and 6.8%, respectively. Thus it was observed that strongly adsorbed water decreases in the order HSO > HMO > HFO, which may be indicative of the binding strength of H_2O (OH groups) (Machenzie and Berggren 1970). Similarly, the infra-red spectra showed OH groups and/or H_2O molecules in HSO and HMO, but not in HFO, heated at 800 °C.

The pore volumes of the prepared materials were 0.136, 0.076 and 0.103 $\mathrm{C\,m^3/g}$ whereas the surface areas were 208, 153, 150 m^2/g for HFO, HSO and HMO respectively.

The particle diameter of the prepared powder were determined using laser diffraction particle size analyzer, Shimadzu, model Sald 2001, Japan. The pore volume measured for the different oxide material shows the increase in the proportion of micro-capillary and micro-pores with

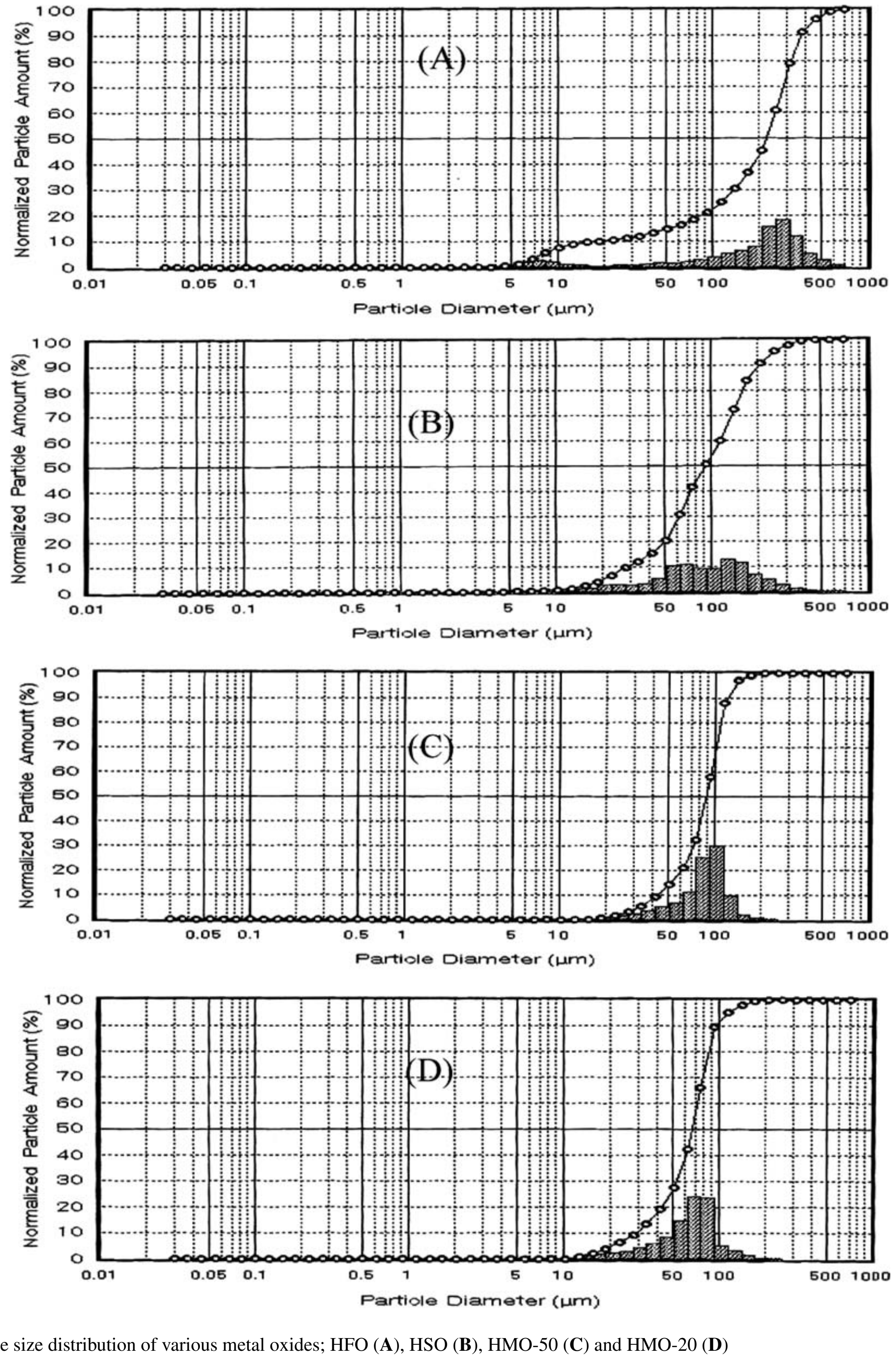

Fig. 1 Particle size distribution of various metal oxides; HFO (**A**), HSO (**B**), HMO-50 (**C**) and HMO-20 (**D**)

increase in the number of substituted stannic metal ions in the mixed oxide. This was confirmed by measurement the average particle diameter of each powder. As shown in Fig. 1, the average particle diameter (micro meter) (X-axis) was determined at the corresponding values at 50% of the Normalized Particle Amount (NPA%) (Y-axis). It

Fig. 2 Plate-type magnetic separator

was found that the average particle diameters at the corresponding values at 50% of NPA were 220, 100, 90 and 60 µm for HFO, HSO, HMO-50 and HMO-20 respectively.

All these facts prove that HMO does not behave as a simple mixture of HFO and HSO and probably show that the mixed oxide is also a hydrous oxide. This mixed oxide has a significant improvement in the physical characteristics (average particle diameter) rather than the individual oxides.

2.7 Plate-type magnetic separator

A plate-type magnetic separator (BIODATA-Diagnostics Company code 62079) was used as permanent magnets for wet magnetic separation. Judging from the number of units installed, this type of magnetic separator represents the most frequently used in various magnetic technologies (Forrest and Rattle 1983). As shown in Fig. 2, a 50 tube magnetic rack was designed to handle magnetic particle experiments. The rack, which is re-usable, contains tube grips to accommodate a variety of tube size. A 50 mg of the samples and 5.0 ml of the reagents are pipetted into the tubes and gently shacked to mix the tube contents. After reaching to complete equilibration the rack is slid into the magnetic separator where each tube is automatically positioned over a cobalt-samarium permanent magnet. The magnetic particles are rapidly and firmly attracted to the bottom of the tubes, and after 20.0 minutes the supernatant in each tube was analyzed and complete decanted from the solid particles that precipitated and bonded to the magnetic base by means of reasonable magnetic force.

Particle magnetization was checked by weighing the amount of the dry solid magnetic materials before and after adding the metal solution. The higher amount of the solid particle that was attracted and bonded to the bottom of the tubes presented the higher particle magnetization.

This technique not only speeds up the whole procedure, by eliminating the handling of individual tubes as well as the centrifugation time, but also helps to maintain sample identification as the tubes stay in one rack throughout the assay.

2.8 Analytical measurement of heavy metals

In the present work, the ion chromatographic (IC) system from Dionex Corporation, Sunnyvale, CA, USA, model 2000i/sp was used. The general components of this instrument including containers for supply of eluent (s), a high-pressure advanced pump to deliver the eluent used, an injector for introducing the sample through the eluent stream to the ion-exchange column.

For inter-separation of several heavy metal ions, the IonPac CS5A analytical column coupled with CG5A guard column are used. These are designed especially for the analysis of transition and heavy metal ions such as lead, cadmium, and zinc ions. Both the column and related guard are packed with divinylbenzene/styrene resin (13.0 µm in diameter) functionalized with both quaternary ammonium and sulfonate functional groups, in layers located on the core of related beads. The cation and anion exchange capacities are 0.071 and 0.033 mequiv./ml of resin, respectively.

A versatile dual-beam absorbance detector UV/VIS was used for measuring in optical wavelength regions ranging from 190 nm to 800 nm.

All measurements are made at room temperature and by using a 50 µl of each test sample. In all cases, the post-column reagent is a mixture of 0.4 mM PAR, 3 M NH_4OH and 1.0 M CH_3COOH, adjusted at pH 9.7 and delivered at a constant flow-rate (0.5 ml/min).

Data processing system for collection and operation of all components in the used system are controlled and organizing by a Dionex AI-450 chromatography software interface via an ACI-2 advanced computer interface.

As shown in Fig. 3(A), Pb, Cu and Cd could be separated well using 80.0 mM oxalic acid as a mobile phase, while Mn is not eluted. Therefore, Mn, Cu and Cd were eluted separately using 7 mM of 2, 6 Pyridine dicarboxylic acid (PDCA) while Pb is not eluted, as shown in Fig. 3(B). Both mobile phases are compatible with CS5A analytical column. Also the effluent from each system could be react with the post-column reagent containing a mixture of 0.4 mM PAR, 3 M NH_4OH and 1.0 M CH_3COOH to

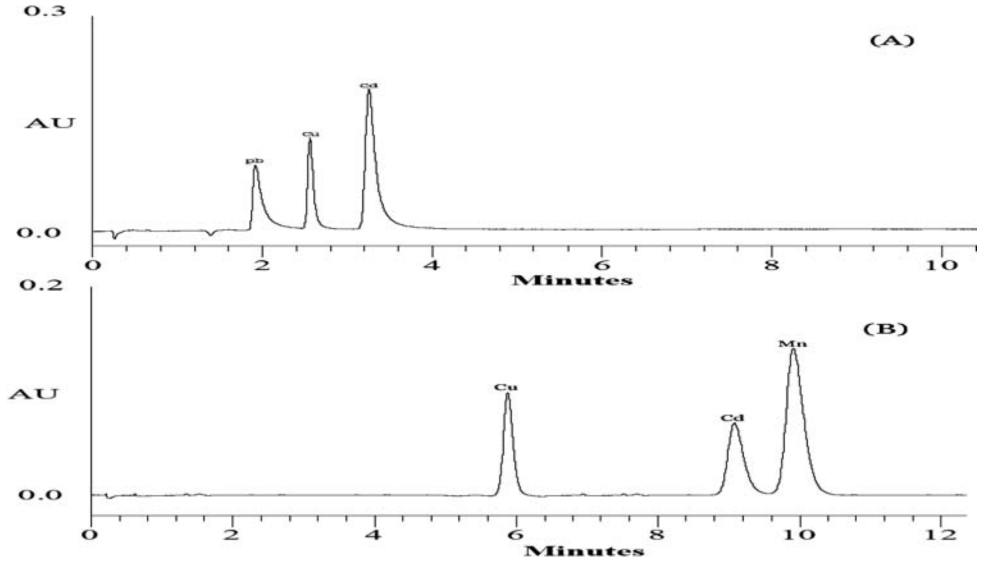

Fig. 3 Elution chromatogram of some heavy metals using CS5A column

form a light absorbing complex. The two elution systems permit a possible measurement of Pb ion in the presence of Mn ion.

Atomic Absorption Spectrophotometry (AAS) of model Z-8100, polarized Zeeman Hitachi, Japan is used as a confirmatory tool as well as for selenium measurement.

3 Results and discussion

Several factors that affect sorption behavior and chemical stabilities of the prepared samples in basic and acid media were carefully evaluated in terms of K_d and uptake percentage. The distribution coefficient was calculated according to the following equation:

$$K_{d(l/g)} = \frac{C_o - C_e}{C_e}\frac{V}{M},$$

where C_o and C_e are the initial and residual metal concentration in the aqueous solution respectively. V is the volume of the solution in liter, M is the weight of the adsorbing materials in gram.

The distribution coefficient of different cation at different concentrations will be elucidated to study the capacity of the new prepared oxides. Besides, the kinetics of sorption of different species on the prepared materials was studied to detect the mechanism of sorption process.

3.1 Effect of agitation time

The sorption rate of Pb (II) and Cd (II) on the four oxide materials are studied at different time intervals ranged from 2 minutes to 24 hrs. The pH-values of the solution were kept at 5.0 and 3.0 for Pb (II) and Cd (II) respectively. As shown in Figs. 4 and 5, the equilibrium time for Pb (II) is reached after 15, 30, 120 and 180 minutes while the equilibrium time for Cd (II) is reached after 20, 60, 60 and 180 minutes for the four investigated oxide HSO, HMO-50, HMO-20 and HFO, respectively. It was observed that faster equilibration was obtained for both Pb (II) and Cd (II) using HSO. The kinetic data indicates that there are highly significant changes in the distribution coefficient of each metal ion using four metal oxides. The uptake percentages of each metal obey the following sequence:

HSO > HMO-50 > HMO-20 > HFO.

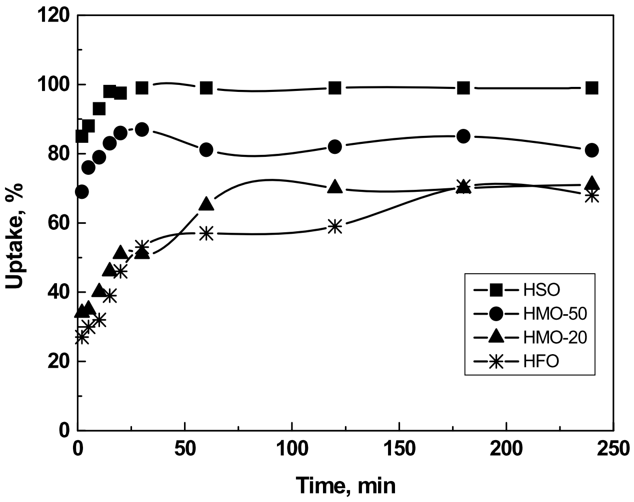

Fig. 4 Effect of agitation time on the uptake percentage of Pb (II) at pH = 5.0

This kinetic order was mainly related to the chemical composition of the prepared oxides which contributing to the chemical reaction of the metal ions in system, i.e. HSO

Table 1 Effect of volume/weight ratio on the distribution coefficient and corresponding capacity of Pb (II) and Cd (II)

V/M	Pb (II)							
(ml/g)	HSO		HMO-50		HMO-20		HFO	
	K_d (L/g)	Capacity (mg/g)	K_d (L/g)	Capacity (mg/g)	K_d (L/g)	Capacity (mg/g)	K_d (L/g)	Capacity (mg/g)
25	31.22	1.24	2.05	1.235	0.312	1.157	0.287	1.15
50	4.95	2.47	0.664	2.32	0.307	2.15	0.244	2.07
100	3.90	4.87	0.430	4.05	0.284	3.7	0.238	3.52
200	0.20	5.06	0.134	4.02	0.084	2.96	0.063	2.4
300	0.10	3.9	0.057	2.4	0.026	1.2	0.033	1.5
500	0.11	4.5	0.055	2.5	0.020	1.0	0.020	1.0
V/M	Cd (II)							
(ml/g)	HSO		HMO-50		HMO-20		HFO	
	K_d (L/g)	Capacity (mg/g)	K_d (L/g)	Capacity (mg/g)	K_d (L/g)	Capacity (mg/g)	K_d (L/g)	Capacity (mg/g)
25	1.760	1.23	1.016	1.22	0.158	1.08	0.071	0.925
50	0.812	2.35	0.373	2.2	0.128	1.80	0.069	1.45
100	0.440	4.07	0.234	3.5	0.097	2.46	0.061	1.9
200	0.157	4.4	0.127	3.9	0.050	2.02	0.035	1.5
300	0.084	3.3	0.026	1.2	0.019	0.93	0.023	1.11
500	0.068	3.0	0.020	1.0	0.012	0.6	0.008	0.4

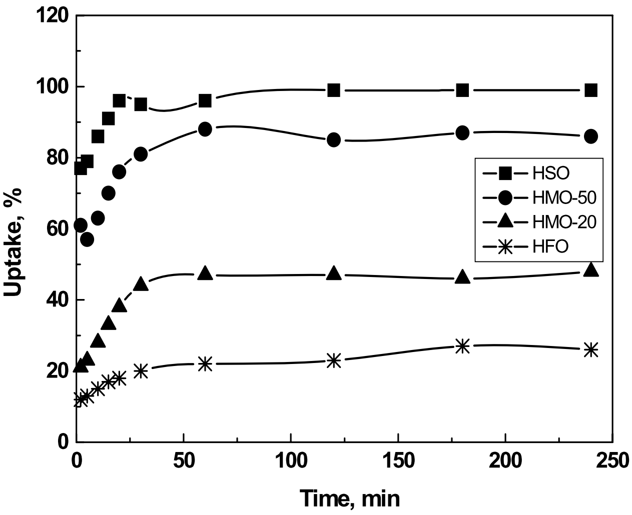

Fig. 5 Effect of agitation time on the uptake percentage of Cd (II) at pH = 3.0

has a highly bounded OH group and hence higher exchange capability which leads to faster steady equilibration. Comparing the two metal ions, it was found that Pb (II) has a relatively higher uptake percentage than that of Cd (II) at the corresponding metal oxide. This is mainly due to the higher exchangeable reactivity of the former with the exchangeable hydrogen atom of the hydroxide group.

3.2 Effect of volume/weight ratio (V/M)

Volume to weight ratio is particularly used to evaluate the minimum amount of solid phase need to be added to achieve the efficient uptake percentage. In this respects, the effect of volume to weight ratio (V/M) on the distribution coefficient of both Pb (II) and Cd (II) metal ions are studied in the range from 25 to 500 (ml/gm).

As shown in Table 1, the distribution coefficient and capacity slightly decreases as V/M increases from 25 up to 100 (ml/gm). For example, the capacity of HSO towards Pb (II) decreases from 0.470 to 0.460 by increasing V/M from 25 to 100 (ml/gm). Starting from V/M equal 100 to 500 (ml/gm), the capacity decreases significantly from 0.460 to 0.085. Thus, the optimum V/M ratio was obtained at 100 (ml/gm) throughout the whole subsequent investigations for both Pb (II) and Cd (II) metal ions.

3.3 Effect of pH

The adsorption of Pb (II) and Cd (II) metal ions was investigated at different values of pH ranging from 2 to 8. The general trend shows that the uptake percentage of both Pb (II) and Cd (II) increases with the increase in solution pH. As shown in Figs. 6 and 7, the maximum uptake percentage was obtained at pH ranged from 5 to 6 and from 4 to 5 for Pb (II) and Cd (II), respectively. These values are

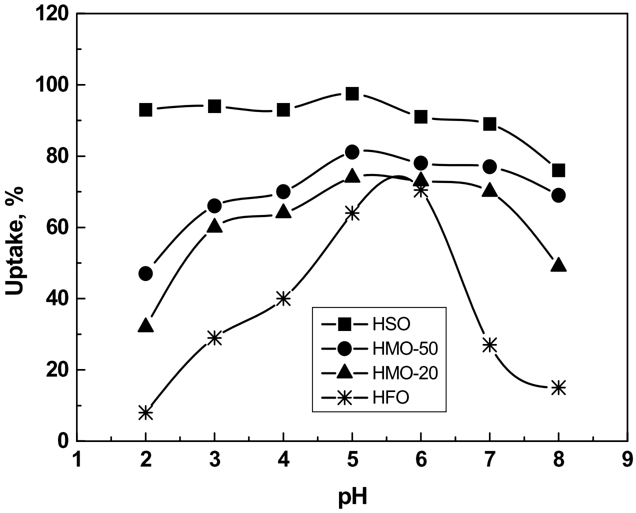

Fig. 6 Effect of pH on the uptake percentage of Pb (II)

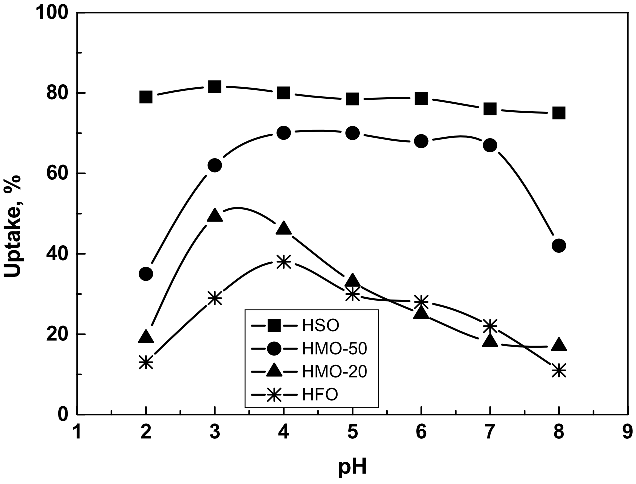

Fig. 7 Effect of pH on the uptake percentage of Cd (II)

close enough to the reported pH's at the point of zero charge (pH_{pzc}) for HSO, HMO and HFO which are equal to 4.4, 6.2 and 6.8, respectively (Ghoniemy et al. 1999; Petro et al. 1987, 1990). By increasing the pH to pH_{pzc} the effective negatively charged (R-OH$^-$) on all oxide surfaces increases, hence the uptake percentage increases. At pH values higher than the pH_{pzc}, the uptake percentage decreases for all the oxides. These mean that the adsorption of Pb (II) and Cd (II) is highly dependent on the surface characteristics at a specific pH-value of the metal solution.

Various interactions between metal ion and amorphous iron oxyhydroxide solid surface could be presented according to the following equations:

$$2\text{R-OH} + \text{M}^{2+} \rightarrow (\text{R-O})_2\,\text{M} + 2\text{H}^+,$$

$$\text{R-OH} + \text{M}^{2+} \rightarrow \text{R-OM}^+ + \text{H}^+,$$

$$\text{R-OH} + \text{M}^{2+} + \text{H}_2\text{O} \rightarrow \text{R-OMOH} + 2\text{H}^+.$$

Based on the previous data, that shows the high dependence of the uptake percentage on the pH value, and according to the previous equation, it could be estimated that the metal ion interaction is performed through ion exchange process rather than site adsorption inside the interior pores of the microporous oxides.

3.4 Isothermal capacities of the prepared magnetizable hydrous oxides

Table 2 shows that the uptake percentage for Pb (II) is generally higher than that for Cd (II). Thus, as shown in Fig. 8, the calculated capacity for Pb (II) is higher than that for Cd (II) at given metal concentration range from 5 to 2000 ppm. The obtained results are in a good agreement with Benjamin and Leckie (1981). They found that for heterogeneous iron oxyhydroxide, the affinity (adsorption bond strength) decreases in the order: Pb > Cu > Zn > Cd. This means that high energy sites for one transition metal ion are low-energy sites for the other.

The capacities of the investigated metal oxides obey the following sequence:

HSO > HMO-50 > HMO-20 > HFO.

This sequence is in a good agreement with the previous uptake sequence. Also, the capacity performance are mainly attributed due to a stronger interaction with the OH groups of the water molecules and/or with the oxygen of the surface OH groups at a certain solution pH (Machenzie and Berggren 1970). However, it could be mentioned that, for HSO, all pore sites may be occupied regardless of the ion exchange process at any pH value. In this respect, high uptake efficiency of HSO with no metal selectivity can be detected at various experimental conditions.

For HFO and HMO, the exchanger process is thus mainly depend on the strength of water binding which is subsequently correlated not only to the oxide acidity (Figs. 6 and 7) but also to the small pore size (Fig. 1).

The high reduction in iron content to 20% leads to significantly low capacity and worsened the requirements for efficient removal by means of plate type magnetic separator.

3.5 Effect of interfering ions

The effect of commonly toxic heavy metals in spiked wastewater sample like Se (VI), Cu (II), and Mn (IV) on the uptake percentages of both Pb (II) and Cd (II) have been studied using various hydrous oxides. As shown in Table 3, the uptake percentages of each of Pb (II) or Cd (II) separately are decreased in the presence of other interfering heavy metals in the mixed wastewater sample. The obtained

Table 2 Effect of metal ion concentration on the distribution coefficient and corresponding uptake percentage of Pb (II) and Cd (II)

Metal conc	Pb (II)							
(ppm)	HSO		HMO-50		HMO-20		HFO	
	K_d (L/g)	Uptake (%)	K_d (L/g)	Uptake (%)	K_d (L/g)	Uptake (%)	K_d (L/g)	Uptake (%)
5	15.49	99.36	11.73	99.15	0.443	81.6	0.669	87
10	9.90	99.0	6.22	98.43	0.440	81.5	0.388	79.6
25	5.45	98.2	0.540	84.8	0.345	77.5	0.316	76
50	3.90	97.5	0.430	81.1	0.284	74.0	0.238	70.5
100	1.01	91.0	0.380	79.17	0.160	61.6	0.112	53
250	0.701	87.5	0.247	71.2	0.062	38.2	0.031	23.7
500	0.308	75.5	0.062	38.5	0.034	25.4	0.012	11.1
1000	0.065	39.4	0.025	20.1	0.014	12.9	0.006	5.84
1500	0.034	25.4	0.015	13.7	0.009	8.9		
2000	0.025	20.0	0.011	10.1	0.007	6.6		
Metal conc	Cd (II)							
(ppm)	HSO		HMO-50		HMO-20		HFO	
	K_d (L/g)	Uptake (%)	K_d (L/g)	Uptake (%)	K_d (L/g)	Uptake (%)	K_d (L/g)	Uptake (%)
5	8.23	98.8	2.31	95.86	0.983	90.78	0.460	82.14
10	1.328	93.0	0.488	83.0	0.340	77.3	0.212	67.9
25	0.751	88.2	0.317	76.04	0.167	62.5	0.110	52.3
50	0.440	81.5	0.234	70.06	0.097	49.2	0.061	38.0
100	0.290	74.36	0.115	53.5	0.058	36.7	0.029	23.0
250	0.146	59.36	0.067	404	0.033	25.2	0.013	15.7
500	0.088	46.8	0.034	25.4	0.016	14.2	0.007	7.4
1000	0.032	24.3	0.017	14.8	0.008	7.5	0.004	3.9
1500	0.017	15.2	0.011	10.1	0.005	4.86	0.002	2.7
2000	0.012	11.5	0.007	7.35	0.003	3.4	0.001	1.9

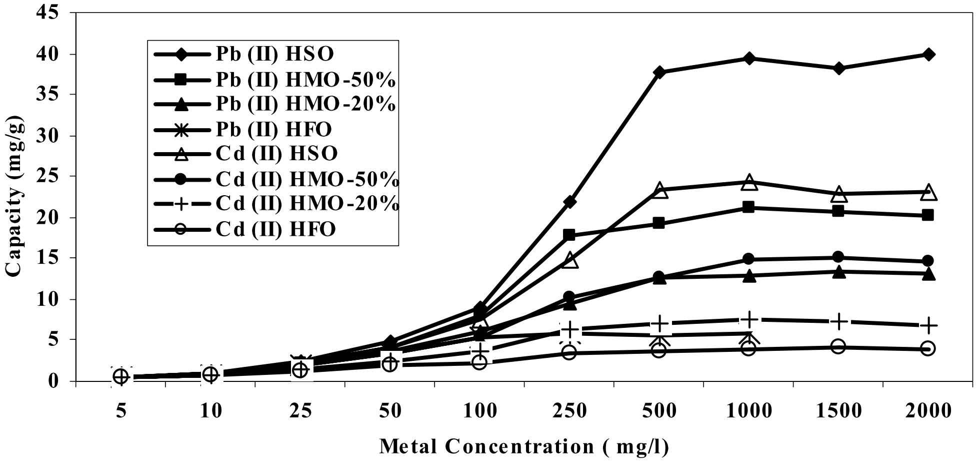

Fig. 8 Isothermal capacity curve of Pb (II) and Cd (II) on various hydrous oxides

behavior reflects a non-specific sorption of toxic heavy metals by using the prepared hydrous oxides. All the prepared hydrous oxides demonstrated high affinity for Pb and Cu, moderate affinity for Cd and Se and low affinity for Mn. The obtained order of selectivity follows the following sequence:

Pb > Cu > Cd > Se > Mn.

Table 3 Effect of interfering metal ions on the uptake percentages of Pb (II) and Cd (II)

Hydrous oxide	Uptake percentages (%)									
	Pb		Cd		Cu		Se		Mn	
	Separate	Mixed	Separate	Mixed	Separate	Mixed	Separate	Mixed	Separate	Mixed
HSO	97.5	72.0	81.5	54.0	–	61.0	–	57.2	–	26.4
HMO-50	81.1	69.6	70.1	42.0	–	56.7	–	50.4	–	22.9
HMO-20	74.0	42.0	49.2	19.2	–	34.6	–	31.1	–	14.8
HFO	70.5	37.0	38.0	13.4	–	27.3	–	23.3	–	9.6

The obtained sequence is most probably due to metal reactivity with exchangeable hydrogen atom of the hydroxide group rather than their adsorption process.

4 Conclusion

Development of the ongoing activity towards the preparation of different magnetic particles of various chemical compositions was successively achieved using simple composite technology, which led to significant cost reduction with economic feasibility. The studies on magnetic composite preparation and heavy metals removal allow the conclusion to be drawn that mixed ferric/stannic oxide revealed satisfactory magnetization and highly efficient treatment capability. This may be attributed to the excellent physical and chemical properties of the mixed oxide that having a particle size of about 60 μm as well as the strong binding strength of the hydroxide group. However, these advantages are counteracted by the small specific surface area. Due to the very small size of mixed hydrous oxide, it can be suspended easily in the wastewater to be treated and then settled down rapidly under the effect of the plate type magnetic separator.

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