Journal of the Taiwan Institute of Chemical Engineers 41 (2010) 585–590

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

The removal of heavy metal ions from spiked aqueous solutions using solid wastes—Comparison of sorption capability

Li-Hua Wang, Chun-I Lin *

Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan

ARTICLE INFO

Article history:
Received 13 July 2009
Received in revised form 17 December 2009
Accepted 17 January 2010

Keywords:
Heavy metals
Solid wastes
Sorption capability

ABSTRACT

The removal of heavy metal ions from spiked aqueous solutions using solid wastes was explored in this work. The sorption capabilities of the sorption agents were compared and evaluation of an agent to replace activated carbon was performed. Experimental results indicated that rice hull ash was effective for sorbing Cd ion; all the solid wastes employed, for removing Cr ion; activated carbon and BF slag for uptaking Cu ion; activated carbon and rice hull ash, for removing Pb ion; activated carbon, activated clay, BF slag and rice hull ash, for abating Ni ion. Rice hull ash was found to be an alternative sorption agent to substitute costly activated carbon for abatement of heavy metal pollution in wastewater.

1. Introduction

Cadmium, chromium, copper, lead and nickel are the most common toxic heavy metal ions contained in industrial wastewater. The toxic effects of these metals in persons are as follows: cadmium associates with renal disfunction and leads to lung disease; chromium can damage kidney, liver, as well as circulatory and nerve tissue; copper can cause anemia, liver and kidney damage, and stomach and intestinal irritation; lead is harmful to the nervous system (World Health Organization, 2006); nickel causes cancer of lungs, nose and bone (Parker, 1980). Therefore, these metals should be removed. Ion exchange, electrolyte or liquid extraction, electrodyalysis, precipitation, cementation, reverse osmosis and adsorption are the methods for treating wastewater containing these metals (Brown *et al.*, 2000; Horacek *et al.*, 1994; Martín *et al.*, 2005b). Among these methods, adsorption by activated carbon has been the most popular technology world wide (Marzal *et al.*, 1996; Mohan and Chander, 2001; Periasamy and Namasivayam, 1994; Shim *et al.*, 2001). Although the sorption efficiency of activated carbon is high, its high cost limits its large scale use, so several waste products from industrial and agricultural operations have been evaluated to replace activated carbon as a sorption agent (Awan *et al.*, 2003; Babel and Kurniawan, 2003; Cheung *et al.*, 2000; Ćurković *et al.*, 1997; Demirbas, 2008; Gupta *et al.*, 2003; Ho and McKay, 1998; Martín *et al.*, 2005b; Periasamy and Namasivayam, 1994; Ricou *et al.*, 1999). Fly ash, the waste from power plant (Gupta and Torres, 1998; Gupta *et al.*, 2003; Héquet *et al.*, 2001; Panday *et al.*, 1985; Ricou *et al.*, 1999), as well as sludge and slag from blast furnace (BF) (Ćurković *et al.*, 2001; Gupta *et al.*, 1997; López *et al.*, 1995, 2003, 2004; López-Delgado *et al.*, 1996, 1998; Martín *et al.*, 2005a,b, 2008), the wastes from iron-making plant and rice hull ash (RHA) (Daifullah *et al.*, 2003) are materials that have been previously studied. However, the potentials of regenerated clay, regenerated form the spent clay of edible oil refining plant, and spent ZnO catalyst, waste from steam reforming plant, have not been investigated. Therefore, the sorption capabilities of these waste materials along with activated carbon and activated clay, the sorption agent usually used in edible oil bleaching, are examined and compared in this investigation.

The sorption capabilities of heavy metals on solids depend on the mechanism of "attachment" on the solid surface. Ion exchange, complexation, surface sorption, chemisorption, sorption-complexation and surface reaction are commonly employed to interpret the way of the "attachment" (Brown *et al.*, 2000). On the other hand, the rates of following three steps affect the overall rate of sorption: metal ion mass transfer in the film outside the particle, intraparticle ion diffusion and "attachment" of ion on solid surface (Panday *et al.*, 1985). The sorption mechanism and the rate of sorption are different for different sorption systems. Therefore, the most probable substitute for activated carbon is searched in this work. After that, the studies on the thermodynamics and the kinetics of that sorption system will be carried out in this laboratory.

* Corresponding author. Tel.: +886 2 2737 6614; fax: +886 2 2737 6644.
E-mail address: cilin@mail.ntust.edu.tw (C.-I. Lin).

1876-1070/$ – see front matter
doi:10.1016/j.jtice.2010.01.005

2. Materials and methods

2.1. Materials

Reagent grade of $Cd(NO_3)_2{\cdot}4H_2O$, $Cr(NO_3)_3{\cdot}9H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $NaNO_3$ and $Pb(NO_3)_2$ were provided by Shimakyu's Pure Chemicals (Osaka, Japan) while $Ni(NO_3)_2{\cdot}6H_2O$, by Kojima Chemicals (Tokyo, Japan).

The aqueous solutions containing heavy metals were prepared by dissolving corresponding nitrate salts ($Cd(NO_3)_2{\cdot}4H_2O$, $Cr(NO_3)_3{\cdot}9H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Pb(NO_3)_2$ and $Ni(NO_3)_2{\cdot}6H_2O$) into deionized water. The ionic strengths of the aqueous solutions were adjusted to 0.1 M by $NaNO_3$. All chemicals used are reagent grade.

The sorption agents employed were: activated carbon (supplied by Acros, New Jersey, U.S.A.), activated clay (Tonsil Optimum 230 FF, provided by P.T.Süd-Chemie, Indonesia), BF slag as well as BF sludge (donated by China Steel Corporation, Kaoshung, Taiwan), fly ash (obtained from Hsin-Da Power plant of Tai Power Corporation, Kaoshung, Taiwan), regenerated clay (regenerated from spent clay in this laboratory), spent clay (generated from a bleaching process and donated by TTET Union Corporateion, Tainan, Taiwan), rice hull ash (calcinated from the rice hull provided by a rice miller in Taichung, Taiwan), and spent ZnO catalyst (containing 80.01 wt% Zn, provided by Taoyuan Refining Plant of Chinese Petroleum Corporation, Taoyuan, Taiwan).

2.2. Pretreatment of sorption agents

Activated carbon, activated clay, BF sludge and spent clay used were not treated before sorption experiments while BF slag, fly ash, regenerated clay, rice hull ash and ZnO catalyst were pretreated.

BF slag was washed by distilled water three times and dried at 105 °C for 24 h. Fly ash was sieved by standard screens of Tyler sieves and grains between 270 mesh and 325 mesh were employed. The regenerated clay was produced by calcinating spent clay at 500 °C under 20 mL air/s for 50 min. Rice hull ash was prepared from rice hull by washing it with distilled water three times, drying at 105 °C for 24 h and then calcinating at 500 °C under 20 mL air/s for 50 min. Spent ZnO catalyst was ground and sieved by the screens mentioned above and the grains between 200 mesh and 250 mesh were used.

The content of Si, Ca, Fe, Mg, Ti, Al, Ba, Cu, Cr, Ni and Cd in the sorption agents were determined by an inductively coupled plasma-mass spectrometer, ICP-MS (Sciex Elan 5000, Perkin Elmer, Thornhill, Ontario, Canada). Average grain diameters of the sorption agents were measured by a laser diffraction particle size analyzer (LS-230, Beckman Coulter, California, USA), while specific surface area, pore volume and average pore diameter were measured by a surface area analyzer (ASIMP-LP-VP2, Quantachrome, Boynton Beach, FL, USA). The morphologies and pH of the sorption agents were observed with a scanning electron microscope (S360, Cambridge, Cambridge, UK) and determined by a pH meter (PHB-9902, Ehun, Taipei, Taiwan), respectively.

Table 1
Experimental conditions for the sorption experiments.

Variable	Value
Initial ionic concentration (M)	0.1
Dosage of sorption agent (10^4 g heavy metal/m^3 solution)	2
Stroke speed (stroke/min)	120
Temperature (°C)	30

2.3. Sorption experiments

Sorption experiments were carried out in a 250 mL high density polyethylene bottle which was immersed in a reciprocal shaking bath (B603D, Hsin An, Taipei, Taiwan). The 50 mL aqueous solution in the bottle was shaken at 120 strokes/min and the temperature was maintained stable for 20 min at 30 °C. Then, 1 ± 0.001 g of sorption agent was loaded into the bottle and the sorption started. After a predetermined time (5–180 min), the sorption was stopped and the slurry was filtered through a piece of 1 μm Advantec filter paper. The concentrations of heavy metals in the aqueous solutions before and after sorption were measured by an atomic absorption spectrometer (AAS6 Vario, Analytic jenaAG, Jena, Germany). The experimental conditions for the sorption experiments are depicted in Table 1.

The percentage sorption of ion was calculated according to the following equation:

$$\text{Percentage sorption of ion}(\%) = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where C and C_0 are the concentrations of metal ion at $t = t$ (instantaneous time) and $t = 0$ in the solution, respectively.

3. Results and discussion

3.1. Characterization of sorption agents

The concentrations of the elements of the sorption agents measured are listed in Table 2, which indicates that silicon is the main component for activated clay, regenerated clay and rice hull ash. Iron is the highest content of metal for activated carbon and BF sludge, while aluminum is the major metal in fly ash and BF slag. Other properties of sorption agents are listed in Table 3. The order of the grain diameter and that of specific surface area of the sorption agents are BF slag > activated carbon > BF sludge > rice hull ash > regenerated clay > activated clay > fly ash > spent ZnO catalyst and activated carbon > activated clay > regenerated clay > rice hull ash > BF sludge > spent ZnO catalyst > fly ash > BF slag, respectively. Activated carbon and rice hull ash have the maximum pore volume and maximum average pore diameter, respectively. Also seen in the table is that activated clay as well as regenerated clay are acidic materials and BF slag as well as rice hull ash are basic materials. The scanning electron images of the sorption agents are shown in Fig. 1, which indicates that the grains

Table 2
Elemental concentrations (ppm) for the sorption agents studied.

	Si	Ca	Fe	Mg	Ti	Al	Ba	Cu	Cr	Ni	Cd
Activated carbon	2630	–	7558	5301	187	2235	118	4.8	47	7.5	ND
Activated clay	28100	610	1940	562	4133	8564	614	16.4	4.5	4.7	–
BF slag	16100	21590	310	15833	2898	21251	545	20	12	5.4	–
BF sludge	2560	2740	37300	2981	655	5962	86	25.7	67	26.1	–
Fly ash	13000	1290	3100	629	9675	15623	1412	84	165	115	–
Regenerated clay	32000	660	2060	573	4953	7613	404	12.7	9.8	2.7	–
Rice hull ash	35450	1200	213	1942	12.8	235	7.3	20.6	ND	16.1	ND
Spent ZnO catalyst	ND	–	ND	ND	ND	ND	ND	774	ND	ND	66.7

ND means concentration is less than that can be detected.