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Removal of Pb(II)ions by Particulate Nanocomposite Prepared via Oxidation-Precipitation and Modified Co-Precipitation Methods

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Abstract: ***Fe:Mn binary oxides was synthesized using a co-precipitation method. A nanoparticles composed of Mn(II)-bearing Fe_3O_4 (Fe:Mn) of ratio that synthesized, giving ahigh specific surfacearea of 314.8 m^2/g at 1:1 ratio. X-Ray Diffraction (XRD) study indicated the formation of nanostructure iron oxide with cubic phase consisting of crystalline structure in 1:0, 7:1 and poorly crystalline structure in 1:1,3:1, 5:1. The influences of Fe:Mn molar ratio. The sorption maximum was observed at a Fe:Mn ratio of 1:1 adsorption capacity was much higher with HA humicacid at the same ratio. adsorption isotherms studied using both Freundlich and Langmuir models it was more suitable for describe adsorption behavior.***

Keywords: binary oxide asnanostructured, oxidation and co-precipitation, adsorption isotherms

1. Introduction

The use of alternative low-costmaterials as potential sorbents for the removal of heavy metalshas been emphasized.Metal oxides have seen increased applications [1].Recently their uses have been further enhanced with the development of nanosized metal oxides to provide a largesurface area and plentiful adsorptive sites [2]. Heavy metals compounds are common pollutants in surface water and ground water, For example, lead ions Pb(II) may cause stomachache, dysphoria, even cancer in human because of their toxicity ,it has been released from awide range of industries[3]. For adsorption of heavy metals from aqueous systems, the most widely studied Nano metal oxide NMOs include iron oxides, manganese oxides, aluminum oxides, and titanium oxides. They are present in different forms, such as particles, tubes and others. The size and shape of NMOs are both important factors to affect their adsorption performance. Efficient synthetic methods to obtain shape-controlled, highly stable, and monodisperse metal oxide nanomaterial. Iron (hydr)oxides are effective for Pb ions adsorption[4]. Manganese oxides are also important scavengers of different anionsThese two materials are both low cost and environmentallyfriendly. It can be anticipated that a Fe: Mn binary oxide originating from the combination of iron oxide and manganese dioxide willhave the potential for Pb(II) ions removal. However, up to now. a series of Fe:Mn binary oxides with different Fe:Mn molar ratios (from 1:0to7:1) were recently synthesized and were tested for Pb removal, a novel adsorbent was prepared byco-precipitation method. NMOsare most commonly environmental friendly and low cost materials. This study investigated the influences of Fe: Mn molar ratio and humic acid content on Pb(II) ions adsorption processes.

2. Preparation of Fe oxide and Fe: Mn binary oxides

All chemicals are analytical grade and were used without further purification. Reaction vessels (glass) were cleaned with 1% HNO_3 and rinsed several times with deionized water before use. All series of Fe:Mn binary oxides was synthesized at different molar ratio(1:0, 1:1, 3:1, 5:1, 7:1 of Fe:Mn). The Fe:Mn binary oxide with a molar ratio of 1:3was prepared according to a method slightly modified from that proposed by G.S. Zhang et al [2]. 0.015 mol Potassium permanganate ($KMnO_4$) (panreacspain) and 0.045 mol iron(II) sulfate heptahydrate ($FeSO_4.7H_2O$) were dissolved in 200 ml of deionized water. Under vigorous magnetic stirring, the $FeSO_4$ solution was added into the $KMnO_4$ solution simultaneously with 4 M NaOH solution to keep the solution pH in a range between 7-8. After addition, the formed suspension was continuously stirred for 1 h, aged at room temperature for 4 h, and then washed repeatedly with deionized water until no sulfate could be detected. The suspension was then filtrated and dried at 65 ˚C for 24 h. The dry material was crushed and stored in a desiccator for later use.

2.1Batch adsorption

Adsorption isotherms of Lead on 1:0, 7:1,5:1, 3:1and 1:1 Fe:Mn binary oxides were obtained using batch experimentsat pH 6.0. Initial concentration varied from 50 mg/Lto 500 mg/L. In each test, 25mg of the adsorbent sample was loadedin the 100ml glass vessel, and 50 ml of Lead solution containing differing amounts of Fe:Mn was then added to the vessel. In order tokeep the pH level around 5-6, 0.1 M of NaOH or HNO_3 was added.The vessels were shaken on an orbit shaker at180 rpm for 5 h at 25 ± 1 ˚C. After the reaction period, all sampleswere filtered by a 0.45 µm membrane filter. The Pb (II) contents were determined

by AAS Atomic Absorption Spectroscopy device. All batch adsorptionexperiments were performed and the results were reported. The influence of humic acid on the sorption ofLead was investigated by (1:1) Fe: Mn molar ratio,5 mg/L of humic acid modified adsorbent and add to a Lead solution when vessels were shaking.

3. Results and Discussion

Fig(1) illustrated the X-ray diffraction patterns of prepared Fe:Mn binary oxides X-Ray Diffraction patterns of Mn−Fe particles were taken on diffractometer with Cu Kα radiation 40 kV and 30 mA. The pattern of the oxide with a Fe: Mn molar ratio of 1:0, namely the pure Fe oxide, shows the orderedline pure Fe oxide pattern with two high broad peaks at 35.4and62.52according to d spacing of 0.253 and 0.148 nm, respectively was magnetite[5,6] .The patterns of Fe:Mn binary oxides with Fe: Mn molar ratios of 7:1, 5:1,3:1, and 1:1 were 7:1 identical to that of the 1:0oxide.Specific surface area (SSA), were determined by nitrogen adsorption−desorption isotherm using the BET method, surface area measurements of the Fe:Mn binary oxides are109.5 , 314.8,311.9,257.2,112.1 of1:0, 1:1, 3:1, 5:1, 7:1(m^2/g) respectively. That all the Fe:Mn binary oxides contain a high surface area than pure Fe oxide[7] and 1:1 molar ratio give a high surface area.

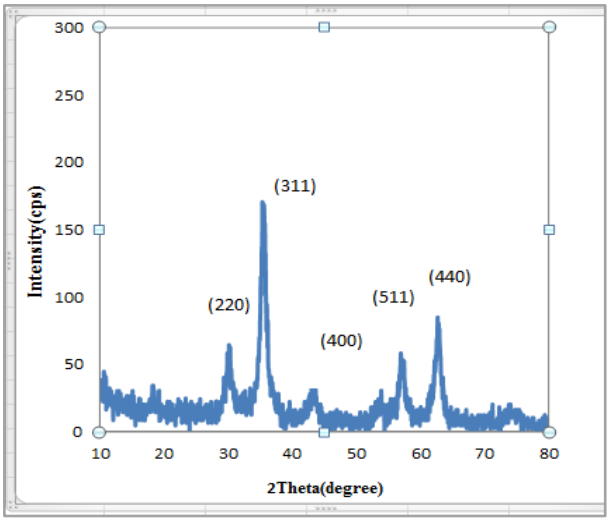

Figure 1: a) The X-ray diffraction of pure Fe oxide

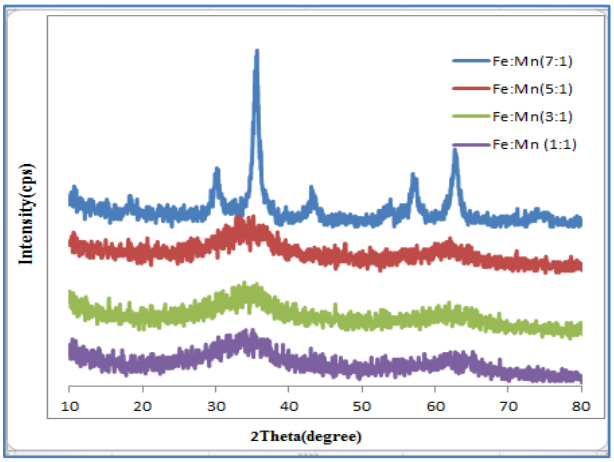

Figure 1: b) The X-ray diffraction ofthe samples synthesized

3.1. Adsorption Capacities and Kinetics

3.1.1. Adsorption data analysis..

Leadsorption capacities of Fe:Mn binary oxides prepared at different Fe:Mn molar ratios were evaluated using adsorption isotherms at pH 5.0 ± 1.0Fig. 2ashows the change of adsorbed Lead as a function of contact time. For initial concentration of 100 mg/l, it is obvious that the adsorption process could be divided into two steps, a quick step and a slow. In the first step, the adsorption rate was fast, and appropriate97% of the equilibrium adsorption capacity was achieved withinthe beginning 3h in 1:1 . This may be due to the fine particles of Fe:Mn binary oxide powders.

The smaller particle size was favorable for the diffusion ofsolution onto the active sites of the solid surface.1:1 had a much higher Pb(II)adsorption capacity than other molar ratio of Fe:Mn (Figure2b). Furthermore, it was very effective in removing Pb(II) at equilibrium concentration. (Adsorption %) and adsorption capacity for adsorbent q_e (mg. g^{-1}), was determined by analyzing Lead before and after the treatment and calculated by using the eq.1. and eq.2

$$\%Adsorption = \frac{C_o - C_e}{C_o} * 100 \quad \text{.....1}$$

$$q_e = \frac{\%Adsorption * C_o}{100} * \frac{V}{W} \quad \text{.....2}$$

where $C_\circ$ and C_e are initial and equilibrium Pb concentrationin the solution (mg L^{-1}), m is the adsorbent dosage (mg), andV is the volume of the solution (mL).

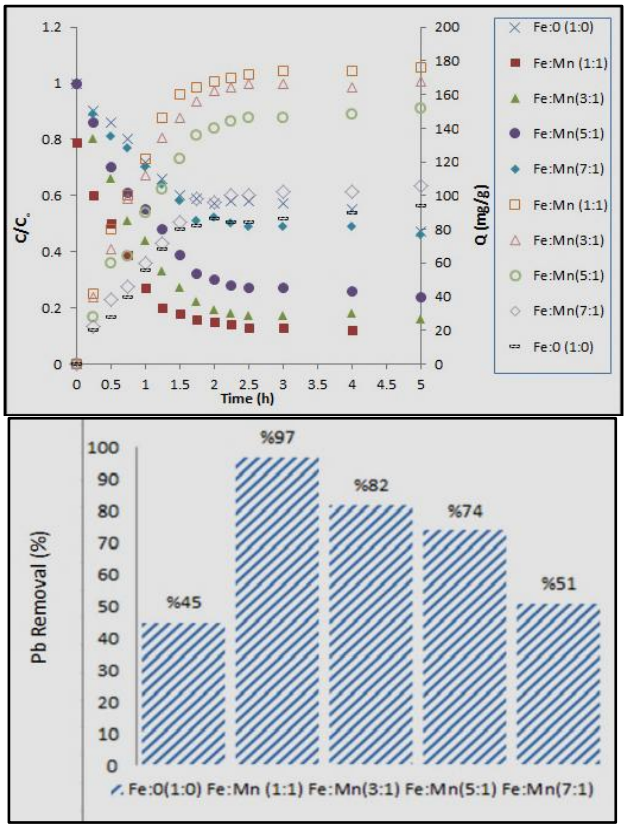

Figure 2: a) Lead adsorption capacity of Fe:Mn binary oxide with the changeof contact time at different molar ratio,b-removal percentage of different molar ratio,

adsorbent dose = 0.5g/L, pH 5.6,speed = 180 rpm, T = 25 ± 1˚C.

The adsorption isotherms of different initial Fe:Mn binary oxides show in figure3The data in Figure 4were fitted into both the Langmuir model (eq3) and Freundlich model (eq4), as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e \quad \text{.....3}$$

$$Log(q_e) = \frac{1}{n} Log(C_e) + Log(K_f) \quad \text{.....4}$$

where q_e (mg/g) is the amount of Pb(II) adsorbed on the adsorbent, C_e (mg/L) is the equilibrium Pb(II) concentrationin solution phase, K_L (L/mg) is the equilibrium adsorptionconstant related to the affinity of binding sites, q_{max} is the maximum amount of the Pb(II) per unit weight of adsorbent for complete monolayer coverage, K_F is roughly an indicator ofthe adsorption capacity, and n is the heterogeneity factor whichhas a lower value for more heterogeneous surfaces.

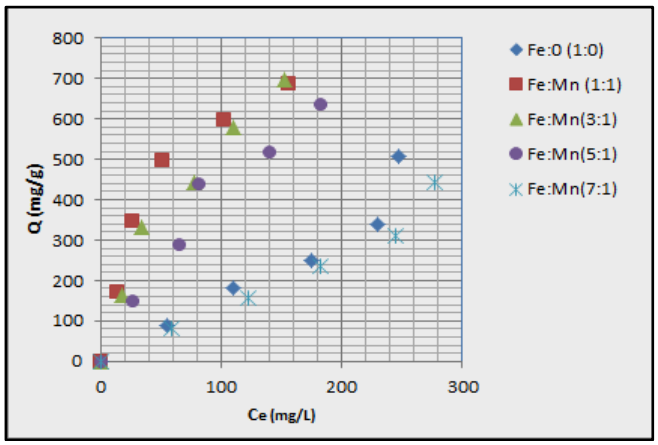

Figure 3: Absorption isotherms of pb(II) on different Fe:Mn molar ratio

As shown in fig 4 and Table 1, the adsorption data of the Fe:Mn(1:1)+HA were better fitted into Freundlich model than Fe:Mn(1:1) This is possibly due to theheterogeneous nature of the adsorbent.

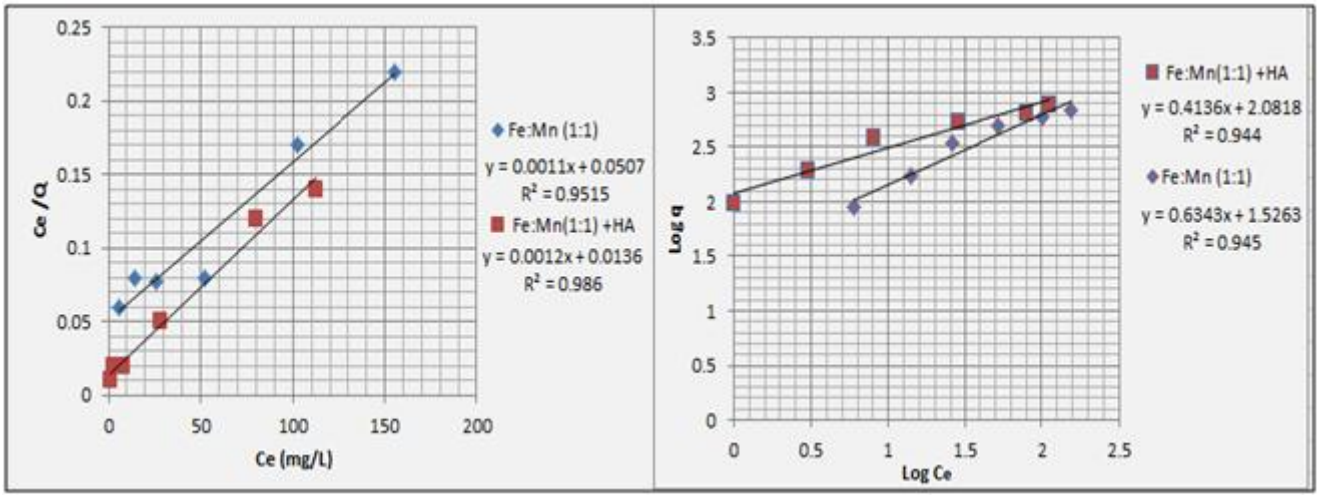

Figure 4: Langmuir and Freundlich adsorption isotherm for pb(II) on onFe:Mn (1:1) and Fe:Mn (1:1)+HA nanocomposite adsorbent dose = 0.5g/L, pH 5±6,speed = 180 rpm, T = 25 ± 1˚C.contact time t= 4h

Table1: Kinetic Parameters for Pb Adsorption on Fe:Mn (1:1) and Fe:Mn (1:1)+HA nanocomposite

adsorbent	Langmuir model			Freundlich model		
	R^2	q(mg/g)	b(L/mg)	R^2	Kf (mg/g)	1/n
Fe:Mn (1:1)	0.95	909	0.02	0.94	33.59	0.63
Fe:Mn (1:1)+HA nanocomposite	0.98	833	0.08	0.94	120	0.41

In contrast, the Langmuir model better described the adsorption behavior of Pb(II) by Fe:Mn (1:1) than Freundlich model. This agreeswith the assumption in the Langmuir model that adsorptionoccurs on a homogeneous surfaceThe maximal adsorption capacity calculated from theLangmuir model was 909 mg/g for Fe:Mn (1:1)and 833mg/g for nanocomposite. This suggests that the humic acid can give the nano particleswith a higher adsorption capacity for Pb(II) due to its excellent surface characteristics. Asshown in Table 2, the magnetic Mn−Fe core has a higher Pb(II) adsorption capacity than magnetic Fe_3O_4, $MnFe_2O_4$ andiron oxide nanoparticle as different adsorbents.

Table 2: Maximum Pb(II) Adsorption Capacities of different Adsorbents

adsorbent	Pb(II) con. range (mg/L)	Pb(II) adsorption capacity (mg/g)	ref
Fe_3O_4	5−350	69.8 (pH 5.0)	8
iron oxide nanoparticles	10−800	35.8(pH 5.5)	9
$MnFe_2O_4$	10−250	69.1 (pH 6.0)	10
Fe_3O_4/MnO_2	5-350	142.0 (pH 5.0)	11
Fe:Mn (1:1)	50-500	909(pH 6.0)	Present study
Fe:Mn (1:1)+HA nanocomposite	50-500	833 (pH 6.0)	Present study

The excellent abilityof MnO_2 for adsorbing Pb(II)[12].leads to maximal sorption capacity in Fe:Mn (1:1)Because high content or equalof MnO_2compare Fe oxide in this ratio for Pb(II) removal that mean when iron oxide little content in ratio.

4. Consolation

A noval Fe:Mn binary oxides as nanoparticles with different Fe: Mn molar ratios were successfully fabricated by oxidation and co-precipitation with high surface area to efficient removal of Pb(II) from water. Batch adsorption technique, The molar ratio of 1:1 exhibited the highest absorption capacity for Pb(II), kinetics and isotherm of Pb adsorption were studied at(50-500)mg/l initial solution pH range from 5-6 on Fe:Mn (1:1) and Fe:Mn (1:1)+HA nanocomposite.

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