INVESTIGATION OF METAL ION BINDING BY AGRICULTURAL BY-PRODUCTS

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ABSTRACT

Oat and wheat straw are abundant yet at the same time are not widely used. For this reason they were tested as metal ion removers from water solutions. Batch experiments were done to determine the affinity of both biomasses for Cu(II), Pb(II), Cr(III), Cr(VI), Ni(II), Zn(II), and Cd(II) metal ions at several pHs; times of reaction and the adsorption capacity for each metal were determined under optimum conditions. The metal ion removal from the biomass was also measured. The batch experiments show that pH 5 was the best pH for adsorption of most of the metal ions, the exception being Cr(VI) (pH 2) in both biomasses. The best adsorption capacities were observed for Pb(II), Cu(II), and Cd(II) for both biomasses. The biomasses were also tested after modification with NaOH to improve their adsorption capacities. The NaOH modification conditions were established by experiments carried out on each biomass. Surprisingly, it was noticed that the drying process during modification affects the adsorption capacity of oat biomass but not wheat biomass. Simultaneous experiments for adsorption capacities of each metal ion were performed by exposing both the unmodified and NaOH modified biomasses to the same environmental conditions. It seems that both biomasses can be employed in heavy metal ion removal processes.

Key words: *oat straw, wheat straw, NaOH, adsorption capacity, metal ion removal*

INTRODUCTION

One of the methods employed for removing contaminants, like heavy metals, from wastewater is adsorption (Al Duri, 1995; Cooney, 1998). The process of adsorption implies the presence of an “adsorbent”: a solid that binds molecules by physical attractive forces, ion exchange, and chemical binding. It is advisable that the adsorbent is available in large quantities, easily regenerable, and economical. Oat and wheat straw (agricultural by-products) could be heavy metal adsorbents which could be selective for some metal ions (Al Duri, 1995). The agricultural by-products metal ion adsorption may involve metal interactions or coordination to functional groups present in natural proteins, lipids, and carbohydrates positioned on cell walls (Drake et al., 1996). Research in the use of agricultural by-products has included metal binding studies with *Datura innoxia*, dyed cellulosic materials, wheat and rice bran, oat fiber, sugarcane bagasse, and sawdust to mention a few (Drake et al., 1996; Shukla and Sakhardane, 1992; Weber, 1996; Laszlo, 1996; Vaishya and Prusad, 1991). Oat and wheat plants have been used as phytoextractors for Zn, Cu, Ni, Pb, and Cd in studies where a soil metal concentration was compared before and after the plants were grown (Dunemann et al., 1991; Idouraine et al., 1996; Chang et al., 1982). This study may generate useful information for the utilization of native agricultural by-products (*Avena monida* and *Triticum delicias*) for the removal of heavy metal ions from wastewater. Not enough information is available for metal removal by these two agricultural by-products.

In this study, oat and wheat metal adsorption capabilities were tested for Pb(II), Cu(II), Cr(III), Cr(VI), Zn(II), Ni(II), and Cd(II) metal ions at several pHs and reaction times. Once the optimum conditions were determined, the adsorption capacities of the unmodified biomasses were determined. In order to increase the adsorption capacity of both biomasses, they were modified at optimal conditions with NaOH. In addition, the effect of freeze drying on metal adsorption during modification was evaluated for both biomasses. Finally, the NaOH modified and unmodified biomasses adsorption capacities were determined for each metal ion.

MATERIALS AND METHODS

Sampling Procedure

The samples were collected from two ranches located in the Juárez Valley during the months of May and June (winter species). Both samples were randomly obtained from the fields. The samples were collected in separate plastic bags. Oat and wheat samples were dried, separately, in an oven at 95°C for one hour. After drying, the samples were ground and sieved to a particle size of 100 mesh.

Profile of pH for Metal Ion Binding

This test required 0.25 g of each biomass. The biomass was washed twice with 40 ml of 0.01M HCl followed by centrifugation (5 minutes at 2900 r.p.m.). The biomass was resuspended in 50ml of 0.01M HCl. The pH of the biomass was adjusted, separately, to 2, 3, 4, 5, and 6. After centrifugation, the supernatants were placed in separate test tubes to determine if they interacted with metal ions. A 0.1mM, metal solution was adjusted to pH 2 and 2 ml of it was reacted with biomass pellets and supernatants. The metal solution pH was then increased and the procedure was repeated for each pH studied. The pellets were reacted for one hour with the metal solution by agitation. The final pH and metal content were measured using a glass pH electrode and a Flame Absorption Atomic Spectrometer (Perkin Elmer, Co.), respectively.

Time Dependency for Metal Ion Binding

A mass of 0.25 g of each studied biomass was used alone. It was washed twice with 0.01M HCl followed by centrifugation. After washing, the biomass was resuspended in 50 ml of deionized water and the pH was adjusted to the optimal binding pH. Three 2ml aliquots of the suspension were placed in three different test tubes. After being centrifuged, the supernatants were discarded and the biomass was reacted with 0.3mM metal solution at the optimal binding pH. Time periods of 5, 10, 15, 30, 60, 90, and 120 minutes were the reaction times tested for adsorption. Final pH and metal content were measured as described above.

Adsorption Capacity for Metal Ion Binding

The capacity experiments were done with 0.1g of each biomass. The biomass was washed twice with 0.01M HCl followed by centrifugation. The washings were kept to determine the mass balance. The biomass was reacted with 0.3mM metal solution at predetermined optimal conditions. Following the optimal reaction time, the supernatants were kept for metal analysis. This mechanism was followed eight times or until the biomass was saturated. After the eight reaction cycles, 2 ml of 0.1M HCl were added to the biomass and reacted again to try to desorb the bound metal ions. The supernatants were kept and the procedure was repeated twice. The final pH of the supernatants and their metal content were measured as described above.

Determination of Optimum NaOH Modification Conditions

Four NaOH concentrations (0.001M, 0.01M, 0.1M, and 1M) were tested. The reaction times were 15 and 30 minutes, and 1,2,3, and 4 hours. The biomass (0.5g) was weighed for each sample. The biomass was then washed twice with 40 ml of 0.1M HCl and twice with deionized water. Each tube was filled with the appropriate NaOH solution and reacted for the predetermined time. After the reaction, the pellets were centrifuged and washed twice with deionized water and then freeze dried. The adsorption capacity was measured for lead as described previously.

Effects of Drying Technique on Metal Binding in Modified Biomasses

Each biomass (0.5g) was placed in three separate centrifuge tubes labeled as freeze drying, oven drying, and four-minute liquid nitrogen exposure followed by oven drying. The biomass was washed and reacted with 0.1M NaOH during 30 minutes of agitation (using a rocker). After being reacted, the samples labeled as freeze-drying were placed in liquid nitrogen for one hour. The samples labeled oven drying were placed in the oven and allowed to dry at 50 °C. The samples labeled freeze drying were placed in a lyophilizer. After the oven drying samples were dried, they were sieved to pass through a 100-mesh sieve. Experiments for Pb(II) adsorption were performed to determine the adsorption capacity of wheat and oat modified biomasses as described previoulsy.

RESULTS AND DISCUSSION

Figures 1 and 2 show that adsorption is pH dependent for all the metals for both biomasses. It is clearly seen that adsorption increases as pH rises for most of the metal ions, except for Cr(VI) ions. The behavior of Cr(VI) may be due to the prevalent forms of this metal complex in acid aqueous systems: acid chromium ($HCrO_4^-$) and chromate (CrO_4^{2-}) ions. Additional experimentation showed that Cr(VI) is reduced to Cr(III) but the reduction process is still unknown (data not shown). The metal adsorption was weakly affected by the reaction time as can be seen in Figures 3 and 4. As time passed, the metal ions remained bound to the biomasses, showing a strong metal-biomass interaction. As observed in the figures, the oat/Cr(III) and wheat/Cr(III) metal affinity increases slightly over time. The ionic radius of chromium is smaller than other metal ions studied. Thus, this may explain this peculiar behavior. It might be possible that the chromium ions diffuse through the biomass pores until being attached to the solid surface (Singh et al., 1992). In order to determine the biomass metal adsorption capacities, the optimum binding pH and reaction time were selected. Table 1 presents a comparison of the adsorption capacity data obtained for each metal by oat and wheat biomasses. The oat biomass interacts strongly with Pb(II) (19.0 mg/g). An interesting feature is the amount of Cr(VI) (4.3 mg/g) and Cd(II) (4.8 mg/g) adsorbed by the oat biomass. Cu(II) and Zn(II) were the most efficiently recovered metals, while both Cr(III) and Cr(VI) were poorly recovered (24% and 24%, respectively). For wheat biomass, Pb(II) also had the highest binding capacity (9.9 mg/g) and most of it was desorbed. Chromium(VI) had the lowest binding capacity for wheat (approximately 0.9 mg/g). Once the adsorption capacity was determined for each metal and biomass, the conditions for optimal NaOH modification were established. Figures 5 and 6 show the effect of biomass modification with NaOH on their adsorption capacity for Pb(II). An increment in adsorption capacities for Pb(II) was observed in oat biomasses which were treated with 1M and 0.1 M NaOH solutions during 1 hour and 30 minutes, respectively (Figure 5). The wheat biomass treated with 0.1M NaOH solution during 30 minutes had the optimum increase in adsorption capacity for Pb(II) (Figure 6). A similar experiment was developed to measure the interaction of Cu(II) with modified biomasses (data not shown). From the Pb(II) and Cu(II) interactions with the modified biomasses it was determined that the best improvement in adsorption capacities occurred when the biomasses were reacted with 0.1M NaOH for 30 minutes. It was also found that freeze drying after modification with NaOH affects the capacity for metal adsorption of the oat biomass (see Figure 7). However, the adsorption capacity of wheat, as shown in Figure 7, was unaffected by the process. The adsorption capacities of the wheat and oat modified biomasses were determined for all of the metal ions studied. When modified and unmodified oat biomasses were compared, an increase in the metal adsorption capacities by the modified biomass was observed for all the metals except Zn(II) and Cd(II) (Table 2). The adsorption capacity of the modified wheat biomass increased for all metal ions except Cu(II) (see Table 3).

In conclusion, oat and wheat biomasses are able to adsorb heavy metal ions and most of them are fully desorbed by treatment with 0.1mHCl. In general, in both biomasses, the adsorption capacities increased when modified with NaOH. The interaction observed between the unmodified biomasses with Cr(VI) may be exploited as an alternative for diminishing the toxicity of Cr(VI). These two biomasses may be considered potential heavy metal adsorbents in wastewater treatment processes.

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Table 1. Metal Adsorption capacities for unmodified biomass.

Metal Ion	Oat			Wheat		
	Amount of Metal Bound (mg/g)	Metal Affinity (μmoles/g)	Percentage of Metal Recovered	Amount of Metal Bound (mg/g)	Metal Affinity (μmoles/g)	Percentage of Metal Recovered
Cu(II)	5.17	81.37	121.15	5	78.69	65.63
Pb(II)	18.97	91.56	94.03	9.9	47.78	95.72
Cr(III)	2.56	49.26	29.77	1.65	31.75	61.93
Cr(VI)	4.29	82.55	24.51	0.88	16.91	87.42
Zn(II)	2.61	39.96	109.71	1.546	23.86	93.01
Ni(II)	3.04	51.78	70.51	2.29	39.01	51.78
Cd(II)	4.76	42.35	77.67	5.23	46.53	59.42

Table 2. Metal adsorption capacities for oat biomass.

Metal Ion	Unmodified			Modified		
	Amount of Metal Bound (mg/g)	Metal Affinity (μmoles/g)	Percentage of Metal Recovered	Amount of Metal Bound (mg/g)	Metal Affinity (μmoles/g)	Percentage of Metal Recovered
Cu(II)	3.14	49.42	106.24	3.46	54.45	108.43
Pb(II)	10.6	51.16	107.7	11.8	56.95	95.88
Cr(III)	2.91	56	25.53	3.34	64.27	22.16
Cr(VI)	1.26	24.25	49.21	2.21	40.41	27.72
Zn(II)	5.89	90.1	38.28	4.07	62.26	59.33
Ni(II)	1.81	30.83	102.76	2.11	35.94	100.11
Cd(II)	6.42	57.12	51.59	5.43	48.31	77.45

Table 3. Metal adsorption capacities for wheat biomass.

Metal Ion	Unmodified			Modified		
	Amount of Metal Bound (mg/g)	Metal Affinity (µmoles/g)	Percentage of Metal Recovered	Amount of Metal Bound (mg/g)	Metal Affinity (µmoles/g)	Percentage of Metal Recovered
Cu(II)	2.9	45.64	116.86	2.51	39.5	121.15
Pb(II)	7.52	36.3	94.72	8.48	40.93	95.09
Cr(III)	1.88	36.18	37.7	1.91	36.75	33.51
Cr(VI)	0.94	18.09	60.00	1.22	23.48	41.96
Zn(II)	1.88	28.76	92.77	2.12	32.43	81.59
Ni(II)	1.22	20.78	121.74	1.83	31.17	86.8
Cd(II)	3.32	29.54	78.35	7	62.28	41.69

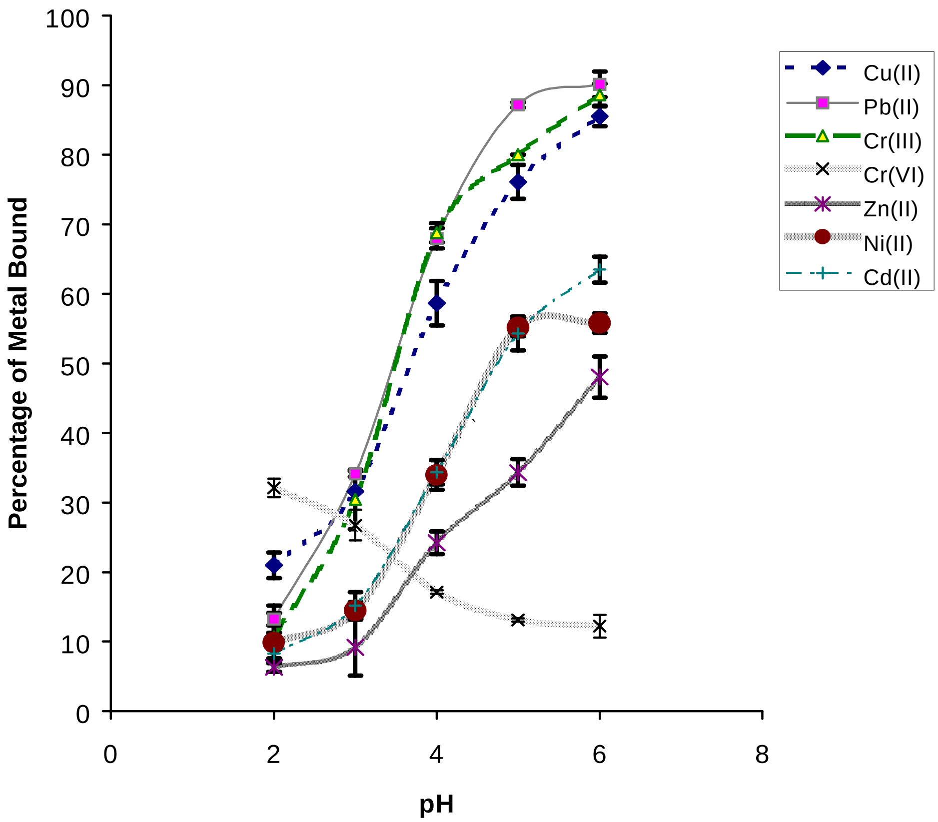

Figure 1. Effect of pH on metal adsorption by oat biomass.

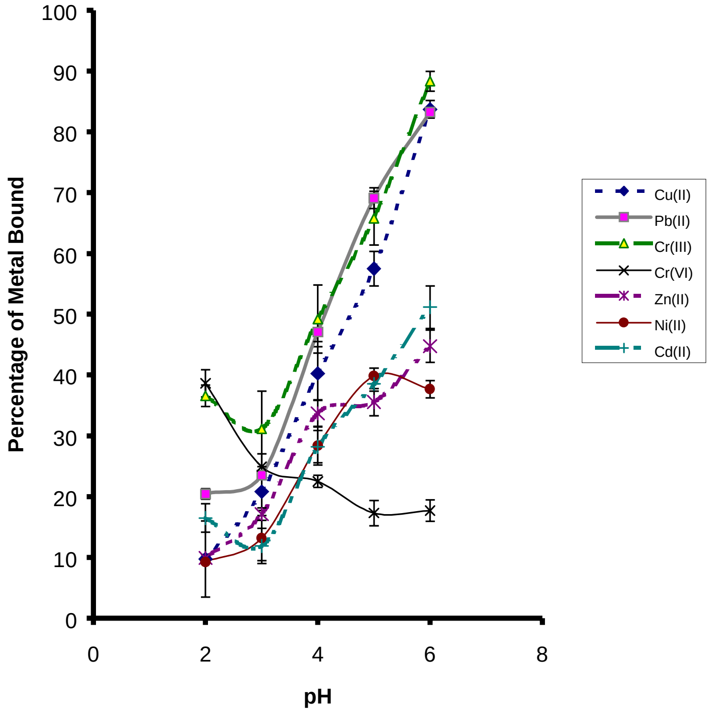

Figure 2. Effect of pH on metal adsorption by wheat biomass.

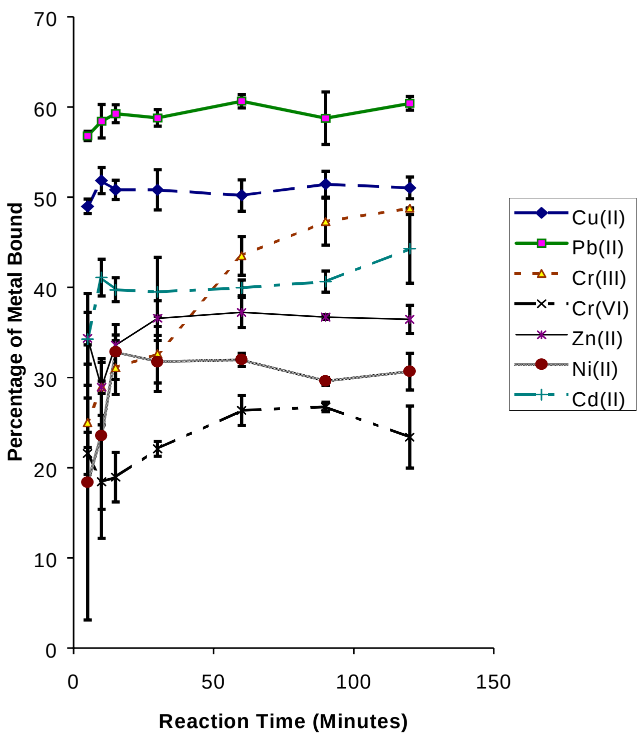

Figure 3. Metal adsorption by oat biomass at different exposure times.

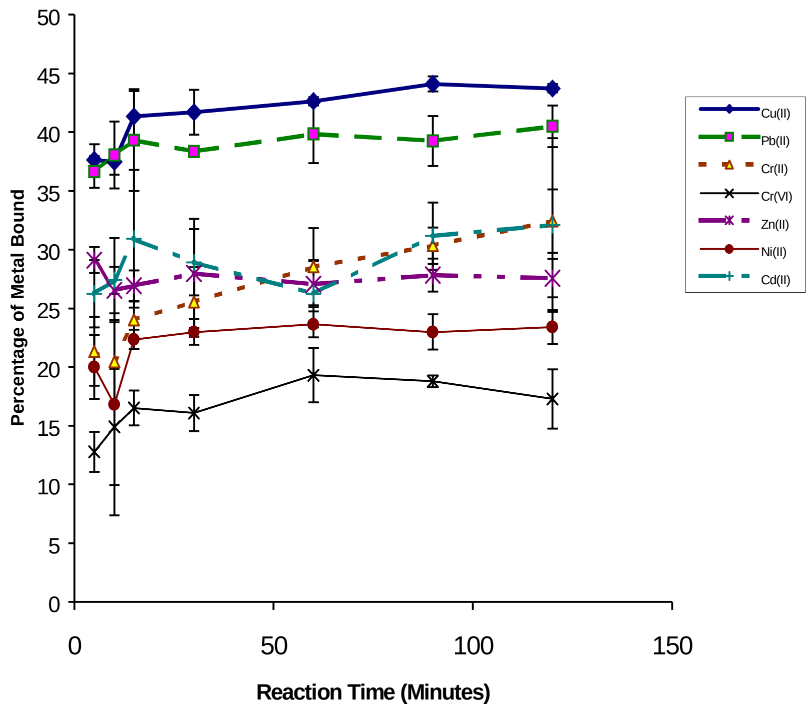

Figure 4. Metal adsorption by wheat biomass at different exposure times.

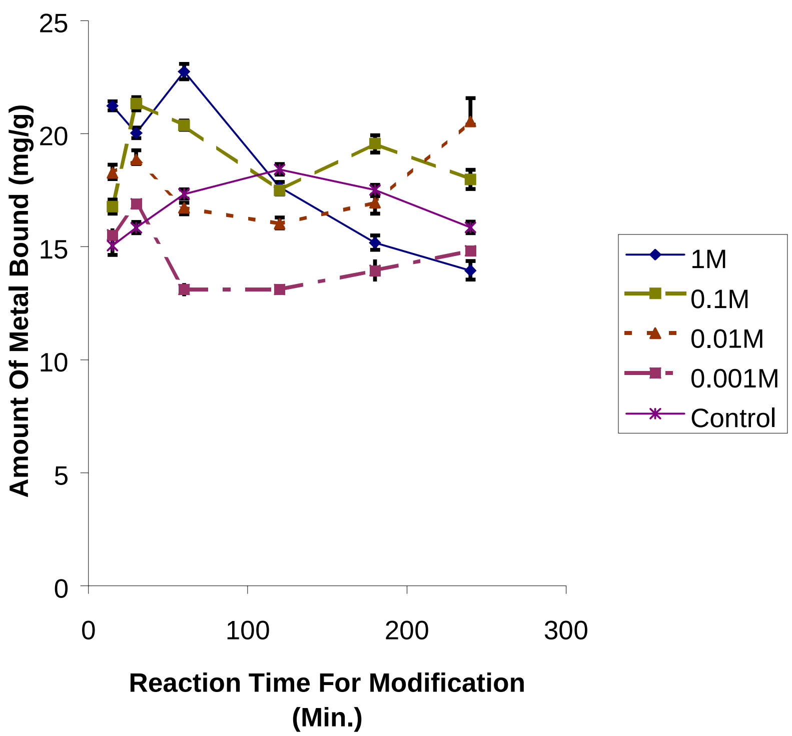

Figure 5. Trend observed for lead adsorption with oat modified biomass. (The biomass was modified separately with four NaOH concentrations.)

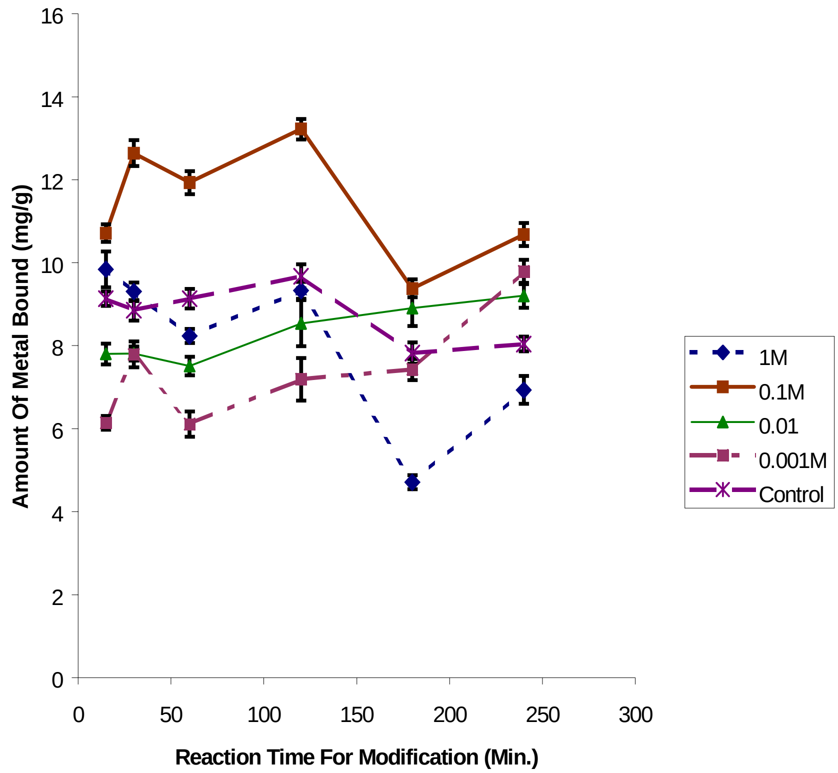

Figure 6. Trend observed for lead adsorption with wheat modified biomass. (The biomass was modified separately with four NaOH concentrations.)

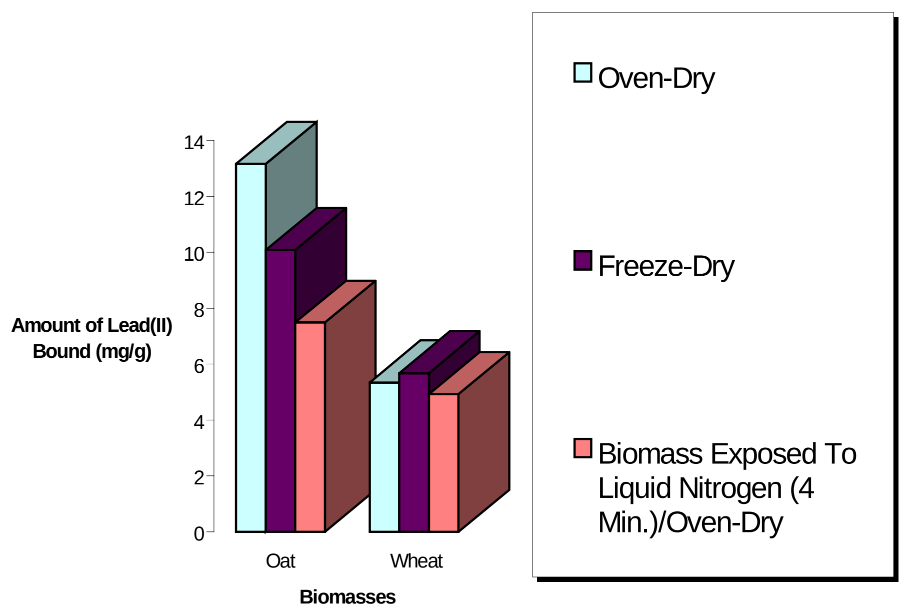

Figure 7. Effect of drying techniques on metal ion adsorption caption by NaOH-modified biomass adsorption capacity.