IMMOBILIZATION OF HEAVY METALS AND STABLE ORGANICS FROM AQUEOUS SYSTEMS ON MODIFIED ACTIVATED CARBON

TUDOR LUPASCU*, MARIA TEODORESCU[2]
** Institute of Chemistry, Academy of Science of Moldova,*
3 Academiei Street, MD 2028 Chisinau, Republic of Moldova.
[2] *National Research and Design Institute for Industrial Ecology-ECOIND, 90-92 Panduri Road, Sector5, 021621 Bucharest, Romania*

Abstract. The negative impact of contamination with heavy metals and stable, hazardous organics, on the one hand and the presence of these contaminants in the human body, on the other hand have been the matter of an increasing concern in the last decades. Exploiting available, although limited resources for designing new methods designated to contaminants' immobilization without generation of additional risk was studied by a Moldavian – Romanian joint team. Active Carbons (AC) obtained from fruit processing waste, as nut shells and plum stones were oxidized to forms with significant ion exchange capacity. The Oxidized Active Carbons (OAC) were characterized and used to selectively adsorb heavy metal ions (as Cadmium – Cd, Copper – Cu and Lead – Pb) or hazardous organics (as ortho-Nitroaniline – ONA). The adsorbent capacity and selectivity was different when adsorbents of different origin were used and also when the adsorption process was applied to mono- or multi-component solution.

Keywords: oxidized active carbon, adsorption, ion exchange, adsorption capacity, selectivity

1. Introduction

The oxidized active carbons (OAC) are known to have a range of valuable properties. They are highly selective complexating ion exchangers, efficient adsorbents, active and selective catalysts of many reactions (L. A. Tarkovskaya and others, 1995).

M.D. Annable et al. (eds.), Methods and Techniques for Cleaning-up Contaminated Sites, 71–79.

The ability of OAC to adsorb cations of metals has been known since 1957 (M. M. Dubinin). It was demonstrated that the adsorptive activity in relation with metal ions is conditioned by the presence of a large quantity of functional groups of acid type on the OAC surface. These groups have different composition and abilities to get ionized. At the interaction of ions, carrying charge of two or three, with the surface of oxidized carbons, besides the exchange of ions, coordinative interaction followed by formation of surface complexes occurs.

The high selectivity of OACs, appearing in numerous systems, determines their successful application to different industrial processes for addressing economical and ecological problems as well as to medicine for adjusting acid-base equilibrium of organism, salt composition of internal medium, etc. (V. I. Davydov and others, 1993).

Besides their above-mentioned properties, OACs have other advantages, as thermal and chemical stability and regenerability (as described by I. A. Taikovskaya in 1981). Thus, the OACs are efficient materials for extracting heavy metals from contaminated aqueous systems.

The oxidized carbons are produced from usual carbons, including active carbons (AC) using treatment with different oxidizing agents, in gaseous or liquid form. The traditional oxidizing agents are nitric (V) acid, ozone, sodium hypochlorite, potassium permanganate, oxygen from air, etc. (process described by H. P. Boehm in 1994).

2. Experimental Work

The laboratory work was directed to:

a. obtaining OAC from fruit seed - based AC;
b. OAC characterization vs. the original AC;
c. adsorption study for heavy metal ions immobilization on OACs;
d. possible use of OAC vs. AC for organics immobilization.

2.1. OAC$_S$ PREPARATION

Active carbons, obtained through traditional methods from peach stones (AC-P) and nut shell (AC-0) were used as the initial material subjected to oxidation.

The oxidation was performed using 50% nitric (V) acid under constant heating (water bath) for 8 hours, using the ratio AC: $HN0_3$=50 g : 150 mL. The resulting samples of the oxidized carbons OAC-P and OAC-0 were washed with distilled water, then consequently treated with 0.1N NaOH (for removal of humic substances and remaining $HN0_3$), then they were washed-up until reaching weak acid reaction. Finally they were dried at 105°C to constant weight.

2.2. OAC$_S$ CHARACTERIZATION

The adsorption capacity, when applied to metal ions, is logically assimilated to ion exchange capacity. The *full exchange capacity* (EC) of OAC was assessed in the reaction with 0.1 N NaOH.

Qualitative and quantitative composition of the surface functional groups was determined by neutralizing them with bases of different strength: 0.05 N solutions of $NaHCO_3$, Na_2C0_3, NaOH and 0.1N HC1 (as Boehm described in 1994 and 1999).

Separation of the functional groups by basicity was carried out taking into consideration the postulate that the solution of $NaHC0_3$ neutralizes strongly acid groups, Na_2C0_3 neutralizes both strongly and weakly acid groups, NaOH neutralizes all carboxylic and phenolic groups.

In order to evaluate the adsorption volume of the OAC samples vs. the corresponding ACs, their adsorption capacities were tested using standard methods. Three chemicals were used: methylene blue, iodine and benzene (excication method). Ion exchange and adsorption characteristics were quantified.

2.3. STUDY OF HEAVY METALS ADSORPTION ON OAC$_S$

Adsorption of Cu, Cd and Pb ions from their 0.01-0.01 M nitrates (V) was studied under static conditions, at the ratio of adsorbent: solution 0.1 g: 25 mL.

Preliminary work was carried to investigate the adsorption kinetics. Although the results obtained demonstrated that the saturation of the oxidized carbons is reached in about 6 hours, the contact of the carbon with the solution lasted for 24 hours to reach equilibrium (standard contact time for adsorption isotherms). After this, the solution was filtered and the equilibrium concentration of ions of the metals was determined.

The equilibrium concentrations of Cu^2+, Pb^2+ and Cd^2+ were determined by the method of oscillopolarography with linearly changing voltage. Oscillopolarogrmmes were registered using an Oscillopolarographer P05122 model 03.

Value of adsorption of ions was calculated by the equation:

$$a = \frac{(C_o - C_e)V}{m} \tag{1}$$

where: a – value of adsorption capacity (meq/g); C_0 – initial concentration of metal ion (meq/mL); Ce – equilibrium concentration (meq/mL); V – volume of solution kept in contact and m – mass of Carbon used (g).

2.4. IMMOBILIZATION OF ORGANICS USING AC_S AND OAC_S

Ortho-Nitroaniline (ONA) was selected as stable, hazardous organic to be immobilized on AC and OAC. The exhausted OAC, after saturation with Pb^{2+} ions was also used as adsorbent.

3. Results and Discussion

The results obtained in the above mentioned experimental work encouraged considering the OAC usage on a larger scale.

3.1. MAIN CHARACTERISTICS OF AC_S VS. OAC_S

Oxidation of the active carbons leads to changes in some characteristics, in relation with both adsorption capacity and structure.

The oxidized carbons OAC-P (plums) and OAC-0 (nut shells) were characterized from the point of view of:

a. Ion exchange capacity (Table 1);
b. Distinguishing between acidic groups of different strength (Table 2) and
c. Adsorption standard characteristics (Table 3).

TABLE 1. Ion exchange characteristics of oxidized active carbon (OAC) and active carbon (AC)

Adsorbent	Ion exchange capacity (EC), meq/g, with				
	0.1 N NaOH	0.05 N NaOH	0.05 N Na_2C0_3	0.05 N NaHCOs	0.1N HC1
OAC-P	3.80	3.30	2.05	1.60	0.18
AC-P	0.80	0.70	0.30	0.20	0.54
OAC-0	4.20	3.40	2.00	1.65	0.27
AC-0	0.40	0.40	0	0	1.06

TABLE 2. Composition of active groups at the surface of OAC and AC

Adsorbent	Quantity of groups, meq/g		
	Carboxylic groups		Phenolic groups
	Weakly acid	Strongly acid	
OAC-P	1.6	0.45	1.25
AC-P	0.2	0.1	0.4
OAC-0	1.65	0.35	1.4
AC-0	0	0	0.4

TABLE 3. Standard adsorption characteristics of OAC and AC

Adsorbent	Adsorption capacity, meq/g		Specific volume, cm^3/g	Surface area, m^2/g
	by Methylene blue	by Iodine	by Methanol	by Methanol
AC-P	330	1231	0.457	900
OAC-P	165	810	0.445	875
AC-0	300	1239	0.4520	1009
OAC-0	210	950	0.456	972

Data given in Table 1 demonstrate that the original carbons (AC) contain a certain amount of functional groups. Anyway, it is to be noticed that the active carbon produced from the peach stones carries mainly acid groups, being thus a cation exchanger, while the active carbon produced from nut shell that carries mainly basic groups is an anion exchanger.

A great number of functional groups of different basicity form at the surface of active carbons during their oxidation with the final result in

- *spectacular increase of acidic group number and*
- *significant decrease of alkaline group number.*

The results presented in Table 2 show that the quantity of acid groups (strong, weak and phenolic) are reasonably comparable for both oxidized sorts of AC.

Data presented in Table 3 demonstrate that the AC oxidation results in decrease in adsorption characteristics: adsorption capacity (as determined using iodine) by 34% for OAC-P and by 24% for OAC-0. Adsorption capacity (as determined by methylene blue) is even more adversely affected: a decreased by 50% for OAC-P and by 30% for OAC-0 was established. These results prove that the porous structure of ACs was affected: part of micropores of active carbons become mesopores which, in their turn, are transformed into macropores. It should be also mentioned that the values of adsorption volume (Vs) and the geometrical surface (surface area, or specific area) of oxidized sorts, compared with the non-oxidized ones (as determined by the adsorption of methanol), although not significantly, are also adversely affected.

3.2. HEAVY MATAL IONS IMMOBILIZATION ON OAC_S

Although the adsorption kinetics (as shown in Figure 1) demonstrate that 6 h is enough time to reach adsorption equilibrium for all three metal ion, the contact was maintained up to 24 h.

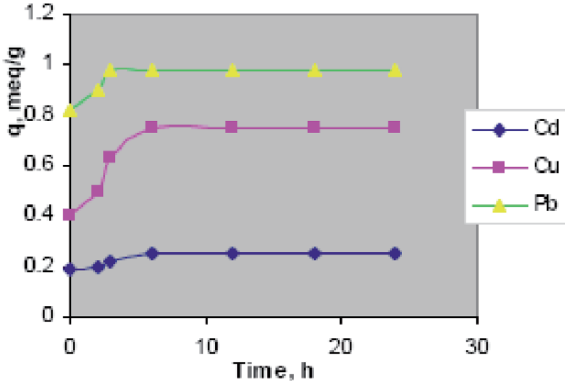

Figure 1. Kinetics of metal ions adsorption from 0.005 M Nitrate solution on Oxidizes Carbons.

Analysis of the adsorption isotherms for metal ions, when immobilized from mono-component solutions shows that the adsorption values for the three studied metals follow the series:

- Cd<Pb<Cu for OAC-P (Figure 2) and
- Cd<Cu<Pb for AOC-0 (Figure 3).

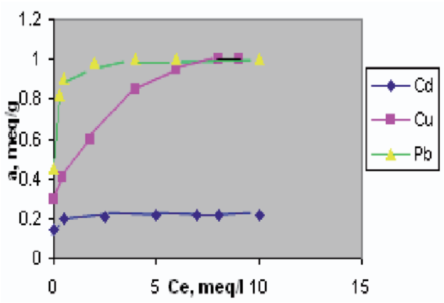

Figure 2. Adsorption Isotherms of metal ions on OAC-P, mono-component soln.

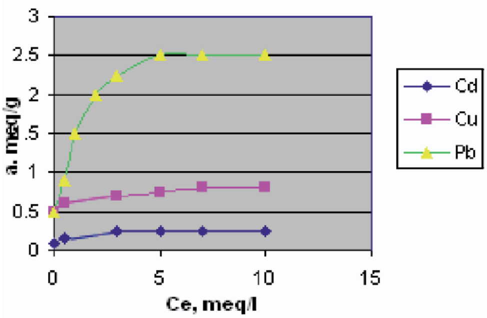

Figure 3. Adsorption Isotherms of metal ions on OAC-0, mono-component soln.

As noticed, values of adsorption capacity (meq/g) are more than double when using OAC-0 than OAC-P, but much lower than the static exchange capacity (EC) of oxidized active carbons (Table 1), i.e. max. 1.2 (for Cu and Pb), vs. 3.8, when adsorbed on OAC-P and max. 2.5 (for Pb), vs. 4.2, when adsorbed on OAC- 0, respectively. A possible explanation for this behavior is the non-availability of some acid groups due to steric barriers. Thus, utilization of 8% of the adsorption potential only was registered for Cd ions and 27% for Cd and Pb, when adsorbed on OAC-0 and 8% for Cd, 27% for Cu and 62% for Pb when OAC-0 was the sorbent.

Analysis of the adsorption isotherms for the same metals ions, when immobilized from their tri-component solution (as nitrates) shows a very interesting behavior:

- The OAC-P selectivity has changed in relation with Cu adsorption: this is worse adsorbed than Cd and the Cu adsorption decreases with the solution concentration increase. In the same time, although the Pb ions adsorbed on OAC-P (Figure 4) from the multi-component solution decreases by 30%, compared with the adsorption value for the mono-component solution, the total adsorption capacity of OAC-P is comparable (about 1 meq/g) with the maximum value for mono-component adsorption.
- A similar behaviour was also found at the adsorption on OAC-0 (Figure 5), except the more severe decrease (about 70%) in the adsorption of Pb ions, a smaller adsorption of Cu (25%), while the adsorption of Cd ions remains the same. It is to be noted that the overall capacity of OAC-0 is about 45% of the best value for the same adsorbent, when used fro mono-component adsorption. The same tendency was noticed in relation with Cu adsorption: the exchange capacity decreases with the solution concentration increase.

Such behaviour changes when the metal ions are adsorbed from their salt mixture are believed to be due to the ions interaction, both in solution and at the interface. This influences the ion ability to displace hydrogen ions in functional groups and also the stability of bounds of pre-adsorbed ions with different groups at the OACs surface.

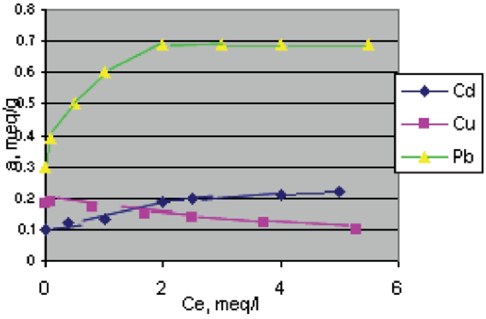

Figure 4. Adsorption Isotherms of metal ions on OAC-P, tri-component soln.

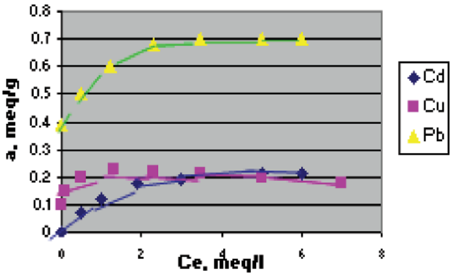

Figure 5. Adsorption Isotherms of metal ions on OAC-0, tri-component soln.

Studying the solution pH and conductibility changes showed that the metal ions immobilization is due in a higher proportion (about 70%) to a direct exchange with H^+ ions (from carboxylic groups) than to the coordinative interactions with oxygen atoms from the oxidized carbon matrix.

3.3. ORGANICS IMMOBILIZATION ON AC AND OAC

Ortho-Nitroaniline (ONA) was selected to investigate its immobilization on both original and oxidized AC (plum stones were the raw material for AC production). The oxidized sort was also used after its previous saturation with Pb^{2+}. The results (Figure 6) were quite contradictory to those obtained for metal ions immobilization.

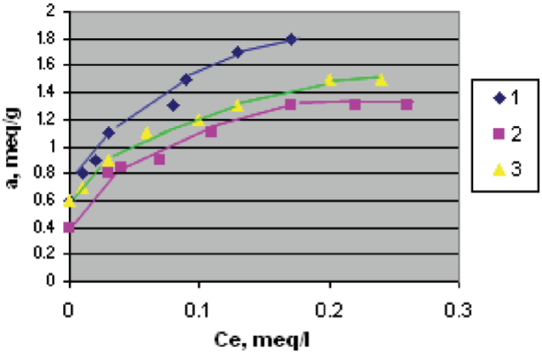

Figure 6. Adsorption Isotherms of ONA on AC (1), OAC (2) and OAC saturated with Pb^{2+} (3).

As shown, the AC adsorption capacity is slightly higher than that of OAC. This is due to the fact that ONA adsorption is driven by physical interactions than the ion exchange process. Changes of AC surface through oxidation, which generates an increased number of acidic functional groups, confer an increased hydrophilic character to OAC. This is not favourable to hydrophobic compounds adsorption. Also, the initial porous structure might have adversely been affected in relation with ONA molecules, too.

The relative increase of OCA adsorption capacity after saturation with lead ions is explained by the role of immobilized metal ions as newly generated active centres that attract (more than reject) the ONA molecule from the aqueous solution.

4. Conclusions

Immobilization of heavy metal ions from their aqueous solutions was successfully done using oxidized active carbons (OACs). The immobilization process was established to have been up to 70% a real ion exchange process than a physical adsorption one.

A significantly different exchange capacity (EC) for OACs was established when the ACs have different origin. The adsorption kinetics and equilibrium were studied vs. heavy metal ions (Pb, Cu, Cd) and hazardous organics (ONA).

An EC decrease of the oxidized sorts was established in relation with heavy metal ions and further decreased capacity was measured for sorption from multi-component solution, although the total capacity may be even higher than the EC itself.

The organic (Ortho-Nitroaniline - ONA) sorption was found to be governed by physical processes and less by chemical/exchange ones and the pre-existing metal ions on the sorption support were in favour of the adsorption process.

Corroborating different results, sometimes apparently contradictory, sustain the fact that every real context needs separate investigation and there are less common rules than factual differences.

Acknowledgement

This paper draws on the joint work done by Physico-chemical Laboratory of the Academy of Science of Moldavia, which carefully prepared the fruit-stone-based active carbons and characterized the adsorbents and to whom the authors are indebted. The work was partially supported by Governmental funds awarded for Academic or National research programmes.

References

L. A. Tarkovskaya and S. S. Stavitskaya. //Ros, *Him. Jurnal Him*., Obsch. D.I. Mendeleeva, 39, 44 (1995).

M. M. Dubinin, "*Poverhnostnde himiceskie soedinenia i ih roll v iavleniah adsorbtii*", Ixd.-vo MGU, Moscow, 1957 p. 9–33.

V. I. Davydov, S. S. Stavitskaya, V. V. Streiko and N. I. Kartel, "*Anterosorbtia: sostoianie, problemd i perspecnvd primenenia*", Naukova Dumka, Kiev, 1993, p. 67.

I. A. Taikovskaya, "*Okislenndi ugoli*", Naukova Dumka, Kiev, 1981, p. 200.

H. P. Boehm, *Carbon,* 32, 759 (1994).

H. P. Boehm, "*Stereohimia i mehanizmd organiceschih reac^ir*", Mir, Moscow, 1968, p. 168–235

Received: March 30, 1999 .