Review Article

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Activated carbons for the removal of heavy metal ions: A systematic review of recent literature focused on lead and arsenic ions

Abstract: This work is a systematic review of the literature over the past decade of the application of activated carbon (microporous or mesoporous) as adsorbents for the removal of heavy metals, focusing especially on lead (Pb) and arsenic (As) ions from the aqueous phase. Classical examples from our lab are also given. Activated carbon is known to provide a high surface area for adsorption. Generally, surface modification is typically required, such as oxidation, treatment with ammonia or even impregnation with ferric ion, etc. and the adsorbent material may originate from various sources. The pristine materials, after modification and those after batch-wise adsorption, were characterized by available techniques (BET analysis, Fourier transform infrared spectroscopy, scanning electron microscopy, thermal analyses, X-ray photoelectron spectroscopy). Adsorption isotherms, thermodynamics and kinetics of the process are also discussed. Selected studies from the literature are examined in comparison with other adsorbents. The role of chemistry in the metals adsorption/removal was investigated.

Keywords: adsorption, lead, arsenic, wastewaters

1 Introduction

The food-chain pyramid receives metals through anthropogenic causes and on top of the pyramid, man receives pre-concentrated metal toxicity. There are also cases of nonanthropogenic pollution. The best known is perhaps that of arsenic in underground well-water in Bangladesh and eastern India, affecting almost 70 million people [56]. As the need for fresh sources of drinking water is becoming urgent worldwide, sustainability in the field of water separation processes and in general, its significance for the chemical and process industry has been noted. It was said that it is particularly interesting to develop an adsorbent demonstrating a high adsorption capacity and low cost for removing various pollutants from contaminated waters; inorganic chemical adsorbents have thus been studied widely, aiming at providing an alternative to activated carbon in the treatment of surface and ground water and industrial effluents [33].

Activated carbons, on the other hand, are among the effective adsorbents because of their excellent sorption capacity. Their use has been often prohibited mainly due to their relatively high cost, low selectivity and regeneration problems; they can be regenerated by thermal desorption of the adsorbed substances or by liquid phase extraction in the case of soluble adsorbed species, although the former method is not very environment-friendly and leads to partial mass loss of the adsorbent [12,16,24,32,48,52,54,63]. The microporous nature of the majority of porous activated carbons is well suited to many applications, including molecular sieving, sorption and catalytic reactions of small molecules. Of course, there are numerous other potential applications, such as sorption of dyes, in which the presence of wider pores, preferably in the mesoporous range, would be advantageous [6]. Metal-loaded mesoporous carbons have been also investigated as efficient adsorbents for organic molecules due to the high mesopore volume as well as to the specific interactions with the supported metals. Therefore, there has recently been a considerable interest in the synthesis of (mesoporous) carbons with high surface areas and tailored pore structures.

Dyes and heavy metals are two contaminants commonly found in the wastewater of several industries. Specifically, heavy metals are discharged by industries

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such as agrochemical, petrochemical and fertilizers, whereas dyes are found principally in effluents of dye manufacturing industries, electroplating factories, distilleries and food companies [30,65]. It was further reported that an anionic dye favored the electrostatic interactions with heavy metals or might create new specific sites for the adsorption process [64].

Another well known metals separation application of activated carbon, apart from organics, is certainly that in gold processing, which however does not constitute a typical case of pollutant removal. Activated carbon, usually in granulated form, has been used to preferentially adsorb gold and silver occurring as cyanide complexes. Powdered activated carbon that offers more surface area for adsorption and is less costly to manufacture, has limitations and difficulties are encountered in its separation; the application of flotation downstream was suggested as an effective separation technique of the loaded particles [71]. Alternative (less toxic) leach solutions to cyanide for gold recovery, such as thiourea in acidic media, has attracted less attention, although the latter presents certain advantages.

Other review articles of the last 5 years of literature exist [10,27,60], however they do not discuss the particular topic of lead and arsenic ions.

2 Adsorbent development

The most widely used carbonaceous materials for the industrial production of activated carbons are coal, wood and coconut shell. These types of precursors are quite expensive and often imported. This makes it necessary, for developing countries, to find a cheap and available feedstock for the preparation of activated carbon for use in industry, drinking water purification and waste water treatment. The term "biomass", according to EU Directive 2003/30/EC, refers to the biodegradable fraction of products, wastes, and residues from agriculture (including vegetable and animal substances), forestry, and related industries, as well as the biodegradable fraction of industrial and municipal waste. Biosorption, a biological method of environmental control can be an alternative to conventional waste-treatment facilities. Several suitable agricultural by-products (lignocellulosics) – i.e. including olive-waste cakes [8], cattle-manure compost [69], bamboo materials [43], apple pulp [23] – have been investigated in the recent years as activated carbon precursors and are still receiving attention.

Activated carbons possess a large surface area, as mentioned above, and different surface functional groups; including carboxyl, carbonyl, phenol, quinone, lactone and other groups bound to the edges of the graphite-like layers. They are therefore regarded as good adsorbents for the removal of heavy metal ions and other inorganic substances, as well as many organic compounds from liquid and gas phases. The production and study of nitrogen-containing activated carbon derived from ammonium humates was the objective of a recent paper [11]. Both surface chemistry and texture of carbons are affected by the nitrogen source and the type of oxygen functionalities pre-existing on the surface [18,19,61]. Acid-base interactions were found to essentially govern the ammonia removal by modified activated carbons [40].

Two synthetic mesoporous carbons, a highly ordered sample with hexagonal structure and a disordered mesoporous carbon, were investigated for the sorption of a dye (Remazol Red 3BS), in comparison to three commercial activated carbons and an hexagonal mesoporous silica with a wormhole pore structure [6]. Mesoporous carbons with three-dimensional pore systems can be prepared from mesoporous silica or silica-alumina templates, such as MCM-48 and KIT-6 (cubic *Ia3d*), KIT-5 (cubic *Fm3m*), SBA-1 (cubic *Pm3n*), SBA-15 and MSU-H (hexagonal *p6mm* with interconnected channels), HMS (wormhole), MCF (foam-like), using mainly sucrose or phenol resin (formed *in situ via* polymerization of phenol and formaldehyde) as carbon source. The resulting carbons exhibit very high specific pore volume and surface area, and tuneable pore diameters with variable framework structures, such as cubic, large cage type, hexagonal, wormhole and foam-like, depending on the structure of the silica template. Furthermore, mesoporous carbons with a high degree of graphitization can be synthesized by the use of appropriate carbon sources, such as acenaphthene, naphthalene, pyrene or anthracene.

Among the low cost adsorbents, chitosan, which is a partially deacetylated polymer of chitin (being slightly soluble at low pH), has a high sorption capacity for several metal ions. Nevertheless, it possesses problems for developing commercial applications [5]; also, the active binding sites of chitosan are not readily available for sorption. So, it was coated on coconut shell carbon [7].

Alginate, a structural component of an algal cell wall, has been also used as a biomolecule immobilization material and has been also shown to be a very potent metal chelator, because it can act as a polyhydroxy- or polycarboxylic acid chelation agent, or as a mixture of both. In this way, an activated carbon-containing alginate bead adsorbent was developed and trialed [55].

The ability of hydrogen peroxide-modified biochar was examined as a filter medium to remove multiple

heavy metals from water. This treatment was conducted in order to increase the oxygen-containing functional groups on adsorbent's surface and thus, enhance its ability for separation removal [68].

Among the surface modification methods applied, functionalization using (anionic) surfactants can significantly enhance the capacities of activated carbons to adsorb heavy metals, such as cadmium. The mechanism by which the surfactant-impregnated activated carbon adsorbs heavy metals was studied [3].

Recent studies revealed that many nano-sized metal oxides exhibited significant sorption capacity and selectivity towards several heavy metal toxic ions. The large specific surface area of activated carbons (from agricultural waste materials origin) was also used to impregnate small or even nano-sized manganese oxide to enhance the suitability of materials in the remediation of an aquatic environment contaminated with copper and lead toxic ions [39].

3 Lead (Pb) ions adsorption

The aim of a recent work [17] was to investigate the effect of oxidation and ammonia, in the form of a solution, on the porosity and surface chemistry of a mesoporous activated carbon material (wood-based, pelletized); so as to identify the types of oxygen or nitrogen functional groups introduced by these treatments, and to examine the resulting modified sorbents regarding their efficiency for the removal of heavy metal ions (i.e. Pb^{2+}) from aqueous solutions. Parts of the carbonaceous material were oxidized with 70% HNO_3 for 4 or 5 hours. The following nomenclature was used for the samples: the initial one was designated as B. The oxidized samples were designated as BNO4, BNO5, respectively, according to the oxidation period. Carbon treatment with aqueous ammonia was performed on carbon materials without preliminary oxidation (products denoted as BNH); and on BNO5 oxidized samples (products denoted as BNONH). Furthermore, oxidation of aminated carbon was also performed (products denoted as BNHNO). The materials exposed to Pb^{2+} have the letter L added to their names (for example, BNH-L, BNHNO-L); lead was, in this case, only taken as the model heavy metal ion.

It is well-accepted that pH is an important factor affecting the sorption of heavy metals and in general, sorption of metallic species increased with increasing pH in a certain range. The effect of pH on Pb^{2+} removal by the adsorbents is shown in Fig. 1. It is also known that lead species in water solution could be present in the
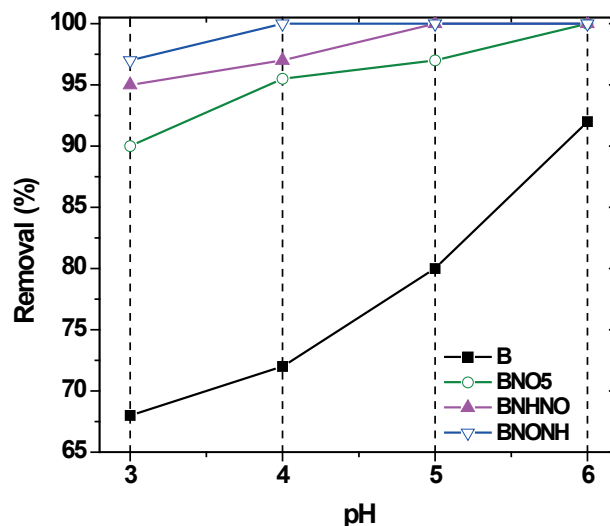

Figure 1: Effect of pH on the adsorption of Pb^{2+} on the carbon samples. Reprinted with permission; copyright Multiscience [17].

forms of Pb^{2+}, $Pb(OH)^+$, $Pb(OH)_2$ and $Pb(OH)_3^-$ at different pH values. The former is the dominant metal species at pH < 7. The distribution of lead species as a function of pH (calculated, for instance, by the Mineql+ software and based on the equilibrium constants), is a helpful basis for discussing the adsorption mechanism. Adsorption of lead was rather attributed to a combination of mechanisms, as discussed below.

Typical adsorption isotherms for the carbon samples were applied (Fig. 2). It was noticed that the correlation coefficients for the Langmuir model at 25°C were higher for B raw carbon and for BNO5, which indicates that this model better describes adsorption on these samples. The values of n were less than unity, indicating that adsorption of lead onto the initial and modified carbon samples was a favorable chemical process. For BNONH and BNHNO, however, the Freundlich model better described the adsorption process, indicating a different adsorption mechanism.

It was also obvious that modification had a well-marked positive effect on the adsorption of Pb^{2+}. Comparison of maximum adsorption capacity values with those reported for other adsorbents are presented in Table 1 [4,22,25,42,49,57,66,67]. For all the investigated adsorbents (except BNHNO), both q_{max} and b values increased with increasing temperature, indicating an endothermic process. For the BNHNO sample, a decrease in adsorption capacity was noticed with the increase of temperature.

The adsorption equilibrium data obtained for the different temperatures were used to calculate the important thermodynamic properties, such as standard Gibbs free
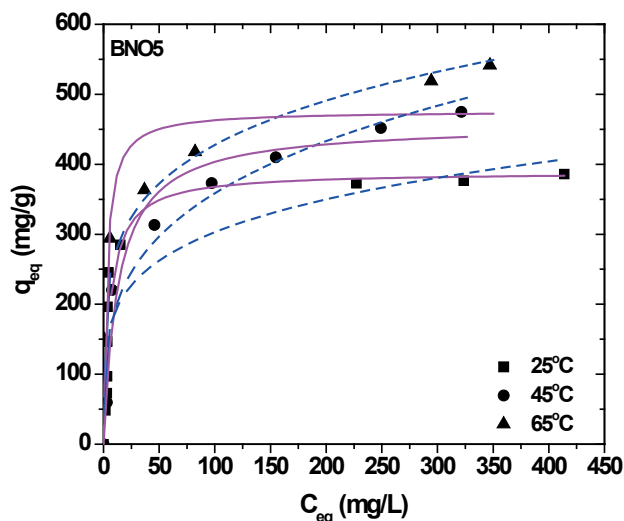
Figure 2: Effect of temperature on lead ion adsorption on one of the prepared/studied samples. Reprinted with permission; copyright Multiscience [17].

Table 1. Adsorption capacities of activated carbons (AC) prepared from various materials towards Pb^{2+} ions. Reprinted with permission; copyright Multiscience [17].

Adsorbent	q_{max} (mg g^{-1})	Reference
EP-activated carbon	146.85	[42]
Sea-buckstone activated carbon	51.81	[49]
Raw CNT	1.66	[66]
Ethylenediamine-modified MWCNT	29.41	[66]
Oxidized MWCNT	25.64	[66]
Cladophora fascicularis	198.5	[22]
Polygonum orientale	98.39	[67]
Coconut shell	76.66	[67]
Iron oxide coated sand	42.4	[57]
Non-living cells *S. cerevisiae*	192.31	[4]
Pyrolusite-modified sewage sludge carbon	69.87	[25]
Oxidised carbon	388.86	sample of our group

energy ΔG^0 standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0). The plot of ΔG^0 versus temperature was found to be linear for all samples. For sample B, BNO5 and BNONH carbon samples, the negative values of ΔG^0 suggested that lead adsorption on these samples was a feasible and spontaneous process. The values became more negative with increasing temperature, indicating higher spontaneity at higher temperatures and better adsorption capacity.

The positive values of ΔH^0 suggested the endothermic nature of the process, which is also supported by the increase of uptake capacity with the increasing temperature, while the negative values of ΔS^0 indicated a greater order of reaction during lead adsorption onto carbon. One of the possible interpretations of endothermicity may be that the ion $[Pb(H_2O)_6]^{2+}$ needs energy to break off the hydration shell and to be accessible for interaction with the surface of carbon. The positive values of ΔS^0 indicated a higher disorder at the interface between the carbon and Pb^{2+} solutions. The fixation of lead ions resulted in a decrease in the freedom of the whole system.

To clearly understand the positive effects of modifications that were applied to carbon in this experiment, the porosity of the lead adsorbents had to be analyzed in detail. As seen, oxidation and treatment with ammonia severely affected the porosity of the materials. Pore volumes and surface areas decreased for all modified samples. This can be attributed to the oxygen functional groups produced, which are deposited in the pores. A significant increase in lead adsorption was observed on those materials, indicating the reaction of the metal ions with these oxygen groups. After adsorption of lead, the textural parameters further significantly decreased, suggesting that a significant part of the pores was occupied by the adsorbate, which was mainly located in mesopores. In these addressed differences, in the modification of carbon support and also the deposition of the adsorbate on its surface, the reaction products could be related to the differences in surface chemistry. Elemental analysis, zeta potential and surface pH results of the initial and oxidized or ammonia-modified carbons were also performed and examined [17].

Some effects of oxidation or ammonia treatment of carbon and then removal of Pb^{2+} were also seen on differential thermogravimetric (DTG) curves that were obtained by adding nitrogen species, where the weight loss was associated to the removal/decomposition of species present on the carbons surface. FTIR spectra measurements also helped in explaining the results for the untreated carbon and oxidized samples. Oxidation led to the formation of new functional groups, such as lactones, carboxylic acid and anhydride, phenol and carbonyl groups. As a result of aqueous ammonia treatment, clear bands were seen that could be related to nitrogen-containing species.

After the oxidation of sample BNHNO, amides got oxidized to nitramines and/or nitrosoamines while amines oxidized to either nitramines or nitrosoamines. The formation of carboxylic groups and also peaks associated with both C=N and C–N of the amine group

were found. The broad band at 1100–1200 cm^{-1} could be attributed to the RCHO and/or R$_2$CO groups that were formed after the oxidation of amines.

For the oxidized sample that was treated with aqueous ammonia (BNONH), the band at 1700 cm^{-1} associated with carboxylic groups disappeared, due to reaction of these groups with ammonium ions. The disappearance of these acidic surface oxide bands confirmed the pH results. This type of interaction corresponded to Brönsted acid-base interactions. Strong indications existed of cation exchange, with carboxylic acid groups being involved in the lead adsorption on the oxidized carbon material.

Taking into account the aforementioned results, the mechanism of adsorption could be demonstrated. For the raw carbon sample, electrostatic forces could be involved in the adsorption process between the negatively charged carbon surface and cationic Pb^{2+} species, because the point of zero charge of this carbon was lower than the adsorption pH (i.e., pH 5). C$_\pi$-cation interactions are mainly due to electrostatic interactions between the quadrupole moment of the aromatic rings of the activated carbon and the metallic cation. It has been further proposed that an unconventional bond may exist between the positive charge (i.e., H$_3$O$^+$ ions) and the delocalized π electrons of the aromatic rings of carbons [66]. Considering the delocalized π electrons as a Lewis base, the interaction between the π electrons and H$_2$O can be described as follows:
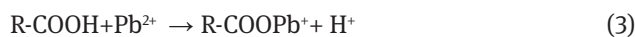
$$-C_\pi + 2H_2O \rightarrow -C_\pi - H_3O^+ + OH^- \tag{1}$$

The cation exchange between $-C_\pi - H_3O^+$ and lead species would thus be a plausible mechanism to account for the observed adsorption of Pb^{2+} on the carbons, at the experimental pH range [59].

$$2(C_\pi - H^+) + Pb^{2+} \rightarrow (C_\pi)_2 + 2H^+ \tag{2}$$

As it could be seen, in the FTIR spectra of all samples after lead adsorption, the intensities of absorption bands at approximately 1630 cm^{-1} were considerably enhanced, which might indicate the additional formation of C=C bonds on the graphene layer of carbon samples. The pH of the residual solution after Pb^{2+} adsorption showed a decrease from 5.00 to 4.26, corroborating the above presented mechanism and indicating a main contribution of this reaction to the overall adsorption process.

On the other hand, taking into account the total acidic groups estimated to be 0.79 mmol g^{-1} after Boehm titration [17] and the maximum adsorption capacity for this carbon sample, which was found to be 0.81 mmol g^{-1},

we can assume that surface acidity is a factor of primary significance. Acidic oxygen-containing groups might behave as ion-exchange sites for the retention of Pb^{2+}-creating metal-ligand surface complexes. In general, the adsorption of Pb^{2+} onto the surface of BNO5 having polar functional groups (–COOH and –OH) could be presented, according to Baniamerian and co-workers [9], as follows:

$$R\text{-COOH} + Pb^{2+} \rightarrow R\text{-COOPb}^+ + H^+ \tag{3}$$

or

$$2(R\text{-COOH}) + Pb^{2+} \rightarrow 2(R\text{-COOPb}^{2+}) \tag{4}$$

and

$$R\text{-}C_6H_5\text{-OH} + Pb^{2+} \rightarrow R\text{-}C_5H_5\text{-OPb}^+ + H^+ \tag{5}$$

The adsorption capacities of the raw, the oxidized BNO5 and the amino-functionalized BNONH samples increased in the temperature range of 25–45°C, while the capacity of the BNHNO carbon decreased, indicating a different adsorption processes and changes in the contribution of appropriate adsorption mechanisms to the overall process, i.e. ion exchange, electrostatic attraction and chemisorption. For this sample after adsorption, the pH dropped by only 0.07 units from 5.00 to 4.93, indicating a different adsorption mechanism. The BNHNO sample was prepared after the oxidation of the BNH sample, and at the surface of BNH, amide and free amino functional groups were present. After oxidation, the amides were oxidized to nitramines and/or nitrosoamines, while amines were oxidized to either nitramines or nitrosoamines. Reoxidation of the carbon surface by NO$_2$ could also occur. Hence, besides the presented adsorption mechanisms for BNO, additional coordination and electrostatic interactions are possible between the Pb^{2+} ions and unprotonated amino groups:

$$R\text{-CONH(CH}_2)_2\text{NH}_2 + Pb^{2+} \rightarrow Pb[R\text{-CONH(CH}_2)_2\text{NH}_2]^{2+} \tag{6}$$
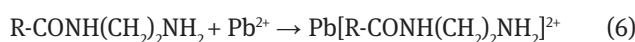
3.1. Other examples for cations

A mercury removal method using polymer-coated activated carbon was studied for possible use in water treatment [36]; in order to increase the affinity of activated carbon for mercury, a sulfur-rich compound, polysulfide-rubber polymer, synthesized by condensation polymerization, was coated onto the activated carbon. The pH effect on mercury removal and adsorption isotherm results indicated competition between protons and mercury for binding to sulfur at low pH. Recently, graphene oxide has

been reported for mercury removal [37]. The large scale production of functionalized graphene at low cost could result in good adsorbents for water purification.

The role of surface functionality on silica and carbonaceous materials for adsorption of cadmium ion was also examined using various mesoporous silicas and activated carbon [45]. Amino-functionalized silica adsorbed greater amounts of Cd(II) than what was adsorbed by either mercapto-functionalized silica or carboxyl-functionalized activated carbon. Modification of the surface structure of adsorbents to enhance their adsorption capacity toward special adsorbates has gained great interest. Introduction of nitrogen functional groups, such as amine, pyridinic and pyrrolic onto the surface of adsorbents and replacing them with oxygen groups is known as one of the modification methods for producing strong adsorbents toward heavy metals, like Cu(II) ion; a new procedure for nitrogenation of commercial activated carbon was proposed [35]. The advantages and limitations of heavy metals sorption (including copper) onto three different carbon materials were presented in another comparison [58].

Earlier, seven inorganic materials, including activated carbon, were examined as sorbents and compared, under similar conditions; the removal of zinc cations and chromate anions from dilute aqueous solutions in batch was investigated [41]. Sorption filters based on different materials were elsewhere tested for their efficiency of removing metals from landfill leachate; to remove a wide range of metals (Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Sr and Zn) and two or more filter materials may need to be combined [47].

Breakthrough curves were plotted for the adsorption of metal ions onto activated carbon, prepared from sawdust, using continuous-flow column operation; an attempt has also been made to model the data generated from these studies using the empirical relationship based on the Adam-Boharts, and Thomas model [34]. A novel carbon material developed by physical activation from waste tire rubber, was used as adsorbent for assessing its removal capacity of lead and nickel ions from aqueous solutions; Langmuir and Dubinin-Radushkevich isotherms helped in indicating the underlying mechanism of the adsorption process [29]. Thermodynamic studies revealed the feasibility and endothermic nature of the system. An activated charcoal, produced from an agricultural waste product (Lapsi seed), was tested for heavy metal ions removal; according to the experimental results the kinetics of the sorption process was found to be pseudo-second order [62].

4 Arsenic (As) ions adsorption

Many researchers have studied the removal of arsenic from aqueous systems using a variety of techniques. Adsorption is a common technology and considered to be effective for the remediation of these species without the production of harmful by-products [21]. Both organic and inorganic compounds of arsenic are reported in natural waters, the latter ones dominate. As(III) dominates in waters (under reducing conditions), as arsenite $(AsO_3)^{3-}$, but in aerobic conditions As(V) is dominant, mainly as $(AsO_4)^{3-}$. Deliyanni and Bandosz [18,19] have investigated the effect of iron oxyhydroxide nanocrystal deposition (doping) in the pore system of carbon. They have also investigated the effect of ammonium carbonate as the precipitating agent and the results indicated that this treatment increased the arsenate sorption capacity.

The activated carbon sample or the oxidized one was impregnated using Fe(III) nitrate and NH_3 as starting solution and precipitating agent, respectively. The latter results in As(V) removal from the aqueous solution [20]. The high affinity of iron oxyhydroxide nanocrystals toward inorganic arsenic species is known. Activated carbon, on the other hand, can provide a high surface area for adsorption. Both the carbon samples before and after (loaded) As(V) adsorption were characterized, in order to explain why the adsorption was improved using this precipitating agent. The adsorption experiments were carried out at pH = 6 and 8, because in tha pH-region the predominate arsenate species are $H_2AsO_4^-$ and $HAsO_4^{2-}$.

Fig. 3 shows the isotherms of the carbons used (Langmuir fitting) both for the initial (non-modified) and oxidized impregnated samples. In this figure, "B" denotes the initial sample, "B1" the oxidized sample (70%
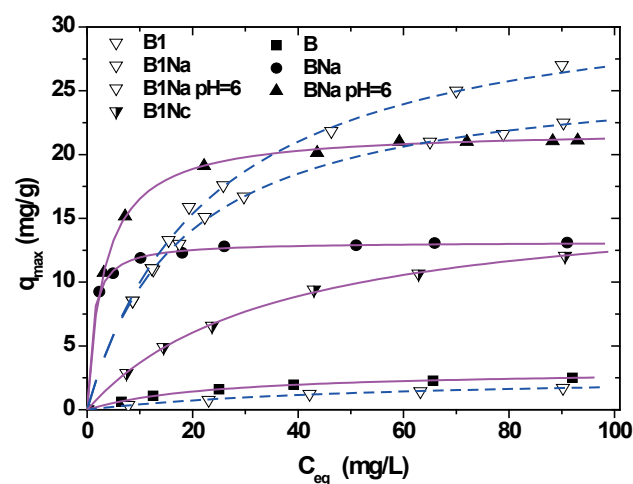

Figure 3: Arsenate adsorption isotherms. Reprinted with permission; copyright Wiley [20].

HNO$_3$), "N" the Fe(III)-impregnated samples, "a" the use of ammonia solution as precipitating agent.

Using a constant adsorbent's dosage of 1 g L^{-1}, B1Na presented adsorption capacity equal to 386.6 mg g^{-1}; that value compared to those of other similar adsorbents reported in literature is considered to be high (Table 2 [13-15,26,28,44,51,53,70]). A possible explanation is the surface chemistry and porosity of those materials which enhanced the arsenic removal.

Table 2: Indicative reported values of maximum arsenic removal. Reprinted with permission; copyright Wiley [20].

| Adsorbent	q_{max} (mg g^{-1})	Reference
Fe-modified AC (concentration up to 20 g L^{-1})	43.6	[14]
Zero-valent Fe on AC	12	[70]
Pretreated peat-based carbon	7.4	[44]
Fe containing mesoporous carbon	7	[28]
Self-manufactured AC from oat hulls	3	[15]
GAC treated with FeCl$_2$	2	[13]
GAC - Fe	1.8	[51]
Oxidized AC treated with FeCl$_2$-FeCl$_3$	0.04	[53]
AC with FeCl$_3$ forced hydrolysis	0.03	[26]
AC impregnated by iron oxyhydroxide	32.86	sample of our group

EDAX maps revealed high dispersion of iron on carbons' surface. The As(V)-loaded samples (those of iron) also presented reduction of the acidity, suggesting reaction of iron oxide/hydroxides with As(V) ions with simultaneous formation of some compounds and salts, such as Fe(AsO$_4$)$_2$, FeAsO$_4$ x Fe(OH)$_3$ and FeAsO$_4$ x H$_2$O [44]. The following reaction was suggested by Mohan and Pittman [50]:

$$FeOOH + 3H_2AsO_4^- \rightarrow Fe\left(H_2AsO_4\right)_3 + 2H_2O \qquad (7)$$

The iron-modified carbon samples of this study intended to introduce iron in the form of iron oxyhydroxide. The latter was extensively discussed in the study of Deliyanni *et al.* [20].

Furthermore, Lewis acid-base interactions were favored by iron interactions, contributing further binding sites for NH$_4^+$ [31]. B1Na presented the highest adsorption capacity in comparison with the other carbon samples. This shows that apart from the reaction of iron oxide/hydroxides with As(V) and the possible formation of salts as reported above, the presence of NH$_4^+$ on the adsorbent's surface had probably some affinity to As(V). According to the pH-effect experiments, it is: pH < pK$_a$ of the NH$_4^+$ ion (as pK$_a$ = 10). Therefore, the ammonium moieties can attract As(V) with strong electrostatic forces, favoring and facilitating the arsenate adsorption:

$$\equiv Fe - OH + R - NH_4^+ + HAsO_4^- \rightarrow$$
$$\rightarrow \equiv Fe - O - AsO_3H...^+NH_4 - R + H_2O \qquad (8)$$
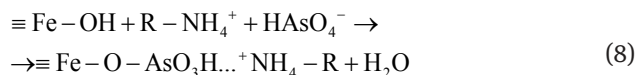
which may further explain the promising removal behavior of the prepared carbon adsorbent, as aforementioned, towards the arsenates.

Based on the above, it was concluded that a meso/microporous carbon surface contributed to changes of arsenic, mainly with the reduction of As(V) to As(III); the latter was also observed with the increased degree of carbon oxidation. Oxidation of the carbon support increased the dispersion of iron oxyhydroxide species on the surface and thus, enhanced the efficiency of arsenate immobilization in the carbon pore system. These species react with arsenate forming salts. Micropores can be characterized as specific nanoreactors having enhanced potential where As(V) can be reduced by carbon surface to As(III) of lower toxicity than that of pentavalent arsenic; As(V) can be reduced to As(III) following reaction with the carbon surface. In addition, the iron doping (impregnation) of activated carbon combined with the precipitation of ammonia, especially on oxidized carbon support, led to ammonium moieties capable of attracting arsenate anionic species by electrostatic forces, resulting in enhanced adsorption capacity.

The use of (i) adsorbents synthesized by the wastes of materials (originated from natural or even synthetic source) or (ii) activated carbons from the same sources has potential economic value. The correct design of such type of adsorbent systems can effectively treat large volume of effluents.

5 Conclusions and regeneration/reactivation perspectives

One of the most crucial factors of activated carbon adsorptive use is its regeneration. While most spent activated carbon used is disposed of, regeneration and reactivation are viable options for industrial facilities and municipalities looking to reduce their carbon footprints or to save money. This is difficult because many problems are generated. At first, the terms "regeneration" and "reactivation" are

often used interchangeably, but they are not the same and in fact they are very different processes [2]. The process of regeneration involves the removal of contaminants from carbon without causing any destruction of it. On the other hand, the process of reactivation utilizes high temperature in a controlled environment to destroy all contaminants [2]. The reactivation process effectively redevelops the pore structure within the carbon to enhance its ability to continue in operation. Usually, the reactivation is used for the reuse of activated carbons. Briefly, spent carbon is reactivated in the same manner as that of its production [1]. In multiple hearth furnaces or rotary kilns, the spent carbon is heated to temperatures above 1700°F utilizing steam as a selective oxidant. Adsorbed organics are either volatilized or pyrolyzed to a carbon char. The high-temperature steam reaction serves to develop the pore volume of the activated carbon and restore its adsorptive capacity [1].

All the above resulted from the need to "save" money using reactivated carbons instead of "fresh" ones, which has associated production cost. The production cost of activated carbons is not the same in USA and Europe. In Europe the cost is usually higher than USA and is estimated to be 0.70–1.50 \$ kg^1 for water treatment (powdered form) [46]. The approximate cost of the reactivated/regenerated carbons use is about 0.70−0.85 \$ kg^1 [46]. A good solution is the turn to carbons sources from low-cost agricultural sources. However, these "green adsorbents" are expected to be inferior (regarding their adsorption capacity) to the super-adsorbents of previous literature (complex materials as modified chitosans, activated carbons, structurally-complex inorganic composite materials etc.), but their cost-potential makes them competitive [38]. So, as it is presented in this review, the adsorption potential of activated carbon is ranged for lead or arsenic removal and depends on the type of activated carbon used each time.

References

[1] http://www.watertechonline.com/articles/activated-carbon-regeneration-or-reactivation (access 28 Aug 2014),

[2] http://www.calgoncarbon.com/products/activated_carbon_reactivation/faq (access 28 Aug 2014),

[3] Ahn C.K., Park D., Woo S.H.,Park J.M., Removal of cationic heavy metal from aqueous solution by activated carbon impregnated with anionic surfactants, J. Hazard. Mater., 2009, 164, 1130-1136.

[4] Amirnia S., Margaritis A.,Ray M., Adsorption of mixtures of toxic metal ions using non-viable cells of saccharomyces cerevisiae, Adsorpt. Sci. Technol., 2012, 30, 43-63.

[5] Amuda O.S., Giwa A.A.,Bello I.A., Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon, Biochem. Eng. J., 2007, 36, 174-181.

[6] Asouhidou D.D., Triantafyllidis K.S., Lazaridis N.K., Matis K.A., Kim S.S.,Pinnavaia T.J., Sorption of reactive dyes from aqueous solutions by ordered hexagonal and disordered mesoporous carbons, Micropor. Mesopor. Mater., 2009, 117, 257-267.

[7] Babel S.,Kurniawan T.A., Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan, Chemosphere, 2004, 54, 951-967.

[8] Baccar R., Bouzid J., Feki M.,Montiel A., Preparation of activated carbon from Tunisian olive-waste cakes and its application for adsorption of heavy metal ions, J. Hazard. Mater., 2009, 162, 1522-1529.

[9] Baniamerian M.J., Moradi S.E., Noori A.,Salahi H., The effect of surface modification on heavy metal ion removal from water by carbon nanoporous adsorbent, Appl. Surf. Sci., 2009, 256, 1347-1354.

[10] Bilal M., Shah J.A., Ashfaq T., Gardazi S.M.H., Tahir A.A., Pervez A., et al., Waste biomass adsorbents for copper removal from industrial wastewater—A review, J. Hazard. Mater., 2013, 263, Part 2, 322-333.

[11] Budaeva A.D.,Zoltoev E.V., Porous structure and sorption properties of nitrogen-containing activated carbon, Fuel, 2010, 89, 2623-2627.

[12] Câmpean A., Tertiş M.,Săndulescu R., Voltammetric determination of some alkaloids and other compounds in pharmaceuticals and urine using an electrochemically activated glassy carbon electrode, Cent. Eur. J. Chem., 2011, 9, 688-700.

[13] Chang Q., Lin W.,Ying W.C., Preparation of iron-impregnated granular activated carbon for arsenic removal from drinking water, J. Hazard. Mater., 2010, 184, 515-522.

[14] Chen W., Parette R., Zou J., Cannon F.S.,Dempsey B.A., Arsenic removal by iron-modified activated carbon, Water Res., 2007, 41, 1851-1858.

[15] Chuang C.L., Fan M., Xu M., Brown R.C., Sung S., Saha B., et al., Adsorption of arsenic(V) by activated carbon prepared from oat hulls, Chemosphere, 2005, 61, 478-483.

[16] Dabioch M., Skorek R., Kita A., Janoska P., Pytlakowska K., Zerzucha P., et al., A study on adsorption of metals by activated carbon in a large-scale (municipal) process of surface water purification, Cent. Eur. J. Chem., 2013, 11, 742-753.

[17] Deliyanni E., Arabatzidou A., Tzoupanos N.,Matis K., Adsorption of Pb^{2+} using mesoporous activated carbon and its effects on surface modifications, Adsorpt. Sci. Technol., 2012, 30, 627-645.

[18] Deliyanni E.,Bandosz T.J., Effect of carbon surface modification with dimethylamine on reactive adsorption of NOx, Langmuir, 2011, 27, 1837-1843.

[19] Deliyanni E.,Bandosz T.J., Importance of carbon surface chemistry in development of iron-carbon composite adsorbents for arsenate removal, J. Hazard. Mater., 2011, 186, 667-674.

[20] Deliyanni E., Bandosz T.J.,Matis K.A., Impregnation of activated carbon by iron oxyhydroxide and its effect on arsenate removal, J. Chem. Technol. Biotechnol., 2013, 88, 1058-1066.

[21] Deliyanni E.A., Peleka E.N.,Matis K.A., Modeling the sorption of metal ions from aqueous solution by iron-based adsorbents, J. Hazard. Mater., 2009, 172, 550-558.

[22] Deng L., Su Y., Su H., Wang X.,Zhu X., Sorption and desorption of lead (II) from wastewater by green algae Cladophora fascicularis, J. Hazard. Mater., 2007, 143, 220-225.

[23] Depci T., Kul A.R.,Önal Y., Competitive adsorption of lead and zinc from aqueous solution on activated carbon prepared from Van apple pulp: Study in single- and multi-solute systems, Chem. Eng. J., 2012, 200-202, 224-236.

[24] Eliyas A.E., Ljutzkanov L., Stambolova I.D., Blaskov V.N., Vassilev S.V., Razkazova-Velkova E.N., et al., Visible light photocatalytic activity of TiO_2 deposited on activated carbon, Cent. Eur. J. Chem., 2013, 11, 464-470.

[25] Fan L., Chen Y., Wang L.,Jiang W., Adsorption of Pb(II) ions from aqueous solutions by pyrolusite-modified activated carbon prepared from sewage sludge, Adsorpt. Sci. Technol., 2011, 29, 495-506.

[26] Fierro V., Muñiz G., Gonzalez-Sánchez G., Ballinas M.L.,Celzard A., Arsenic removal by iron-doped activated carbons prepared by ferric chloride forced hydrolysis, J. Hazard. Mater., 2009, 168, 430-437.

[27] Fu F.,Wang Q., Removal of heavy metal ions from wastewaters: A review, J. Environ. Manage., 2011, 92, 407-418.

[28] Gu Z., Deng B.,Yang J., Synthesis and evaluation of iron-containing ordered mesoporous carbon (FeOMC) for arsenic adsorption, Micropor. Mesopor. Mater., 2007, 102, 265-273.

[29] Gupta V.K., Ganjali M.R., Nayak A., Bhushan B.,Agarwal S., Enhanced heavy metals removal and recovery by mesoporous adsorbent prepared from waste rubber tire, Chem. Eng. J., 2012, 197, 330-342.

[30] Hernández-Montoya V., Mendoza-Castillo D.I., Bonilla-Petriciolet A., Montes-Morán M.A.,Pérez-Cruz M.A., Role of the pericarp of Carya illinoinensis as biosorbent and as precursor of activated carbon for the removal of lead and acid blue 25 in aqueous solutions, Journal of Analytical and Applied Pyrolysis, 2011, 92, 143-151.

[31] Huang C.-C., Li H.-S.,Chen C.-H., Effect of surface acidic oxides of activated carbon on adsorption of ammonia, J. Hazard. Mater., 2008, 159, 523-527.

[32] Jasiñska J., Krzyžyñska B.,Kozłowski M., Influence of activated carbon modifications on their catalytic activity in methanol and ethanol conversion reactions, Cent. Eur. J. Chem., 2011, 9, 925-931.

[33] Jiang J.Q.,Ashekuzzaman S.M., Development of novel inorganic adsorbent for water treatment, Curr. Opinion Chem. Eng., 2012, 1, 191-199.

[34] Kalavathy M.H., Karthikeyan T., Rajgopal S.,Miranda L.R., Kinetic and isotherm studies of Cu(II) adsorption onto H3PO 4-activated rubber wood sawdust, J. Colloid Interface Sci., 2005, 292, 354-362.

[35] Kasnejad M.H., Esfandiari A., Kaghazchi T.,Asasian N., Effect of pre-oxidation for introduction of nitrogen containing functional groups into the structure of activated carbons and its influence on Cu (II) adsorption, J. Taiwan Inst. Chem. Eng., 2012, 43, 736-740.

[36] Kim E.A., Seyfferth A.L., Fendorf S.,Luthy R.G., Immobilization of Hg(II) in water with polysulfide-rubber (PSR) polymer-coated activated carbon, Water Res., 2011, 45, 453-460.

[37] Kyzas G.Z., Deliyanni E.A.,Matis K.A., Graphene oxide and its application as an adsorbent for wastewater treatment, J. Chem. Technol. Biotechnol., 2014, 89, 196-205.

[38] Kyzas G.Z.,Kostoglou M., Green adsorbents for wastewaters: A critical review, Materials, 2014, 7, 333-364.

[39] Lalhmunsiama, Lee S.M.,Tiwari D., Manganese oxide immobilized activated carbons in the remediation of aqueous wastes contaminated with copper(II) and lead(II), Chem. Eng. J., 2013, 225, 128-137.

[40] Le Leuch L.M.,Bandosz T.J., The role of water and surface acidity on the reactive adsorption of ammonia on modified activated carbons, Carbon, 2007, 45, 568-578.

[41] Lehmann M., Zouboulis A.I.,Matis K.A., Removal of metal ions from dilute aqueous solutions: A comparative study of inorganic sorbent materials, Chemosphere, 1999, 39, 881-892.

[42] Li Y., Du Q., Wang X., Zhang P., Wang D., Wang Z., et al., Removal of lead from aqueous solution by activated carbon prepared from Enteromorpha prolifera by zinc chloride activation, J. Hazard. Mater., 2010, 183, 583-589.

[43] Lo S.-F., Wang S.-Y., Tsai M.-J.,Lin L.-D., Adsorption capacity and removal efficiency of heavy metal ions by Moso and Ma bamboo activated carbons, Chem. Eng. Res. Des., 2012, 90, 1397-1406.

[44] Lorenzen L., van Deventer J.S.J.,Landi W.M., Factors affecting the mechanism of the adsorption of arsenic species on activated carbon, Miner. Eng., 1995, 8, 557-569.

[45] Machida M., Fotoohi B., Amamo Y., Ohba T., Kanoh H.,Mercier L., Cadmium(II) adsorption using functional mesoporous silica and activated carbon, J. Hazard. Mater., 2012, 221-222, 220-227.

[46] Marsh H.,Reinoso-Rodriguez F.: 2012, Activated carbon, London, UK, Elsevier.

[47] Modin H., Persson K.M., Andersson A.,van Praagh M., Removal of metals from landfill leachate by sorption to activated carbon, bone meal and iron fines, J. Hazard. Mater., 2011, 189, 749-754.

[48] Mohammadi S.Z., Karimi M.A., Afzali D.,Mansouri F., Preparation and characterization of activated carbon from Amygdalus Scoparia shell by chemical activation and its application for removal of lead from aqueous solutions, Cent. Eur. J. Chem., 2010, 8, 1273-1280.

[49] Mohammadi S.Z., Karimi M.A., Afzali D.,Mansouri F., Removal of Pb(II) from aqueous solutions using activated carbon from Sea-buckthorn stones by chemical activation, Desalination, 2010, 262, 86-93.

[50] Mohan D.,Pittman Jr C.U., Arsenic removal from water/wastewater using adsorbents-A critical review, J. Hazard. Mater., 2007, 142, 1-53.

[51] Mondal P., Majumder C.B.,Mohanty B., Effects of adsorbent dose, its particle size and initial arsenic concentration on the removal of arsenic, iron and manganese from simulated ground water by Fe3+ impregnated activated carbon, J. Hazard. Mater., 2008, 150, 695-702.

[52] Moreno-Piraján J.C.,Giraldo L., Activated carbon from bamboo waste modified with iron and its application in the study of the adsorption of arsenite and arsenate, Cent. Eur. J. Chem., 2013, 11, 160-170.

[53] Muñiz G., Fierro V., Celzard A., Furdin G., Gonzalez-Sánchez G., Ballinas M.L., Synthesis, characterization and performance in arsenic removal of iron-doped activated carbons prepared by impregnation with Fe(III) and Fe(II), J. Hazard. Mater., 2009, 165, 893-902.

[54] Nowicki P., Kuszyńska I., Przepiórski J.,Pietrzak R., The effect of chemical activation method on properties of activated carbons obtained from pine cones, Cent. Eur. J. Chem., 2013, 11, 78-85.

[55] Park H.G., Kim T.W., Chae M.Y.,Yoo I.K., Activated carbon-containing alginate adsorbent for the simultaneous removal of heavy metals and toxic organics, Process Biochem., 2007, 42, 1371-1377.

[56] Peleka E.N.,Matis K.A., Water separation processes and sustainability, Ind. Eng. Chem. Res., 2011, 50, 421-430.

[57] Phuengprasop T., Sittiwong J.,Unob F., Removal of heavy metal ions by iron oxide coated sewage sludge, J. Hazard. Mater., 2011, 186, 502-507.

[58] Pyrzyńska K.,Bystrzejewski M., Comparative study of heavy metal ions sorption onto activated carbon, carbon nanotubes, and carbon-encapsulated magnetic nanoparticles, Colloid Surf. A., 2010, 362, 102-109.

[59] Rivera-Utrilla J.,Sánchez-Polo M., Adsorption of Cr(III) on ozonised activated carbon. Importance of Cπ—cation interactions, Water Res., 2003, 37, 3335-3340.

[60] Rivera-Utrilla J., Sánchez-Polo M., Gómez-Serrano V., Álvarez P.M., Alvim-Ferraz M.C.M.,Dias J.M., Activated carbon modifications to enhance its water treatment applications. An overview, J. Hazard. Mater., 2011, 187, 1-23.

[61] Seredych M., Hulicova-Jurcakova D., Lu G.Q.,Bandosz T.J., Surface functional groups of carbons and the effects of their chemical character, density and accessibility to ions on electrochemical performance, Carbon, 2008, 46, 1475-1488.

[62] Shrestha R.M., Varga I., Bajtai J.,Varga M., Design of surface functionalization of waste material originated charcoals by an optimized chemical carbonization for the purpose of heavy metal removal from industrial waste waters, Microchem. J., 2013, 108, 224-232.

[63] Şváb M., Sukdolová K.,Şvábová M., Competitive adsorption of toxic metals on activated carbon, Cent. Eur. J. Chem., 2011, 9, 437-445.

[64] Tovar-Gómez R., Rivera-Ramírez D.A., Hernández-Montoya V., Bonilla-Petriciolet A., Durán-Valle C.J.,Montes-Morán M.A., Synergic adsorption in the simultaneous removal of acid blue 25 and heavy metals from water using a Ca(PO 3) 2-modified carbon, J. Hazard. Mater., 2012, 199-200, 290-300.

[65] Treviño-Cordero H., Juárez-Aguilar L.G., Mendoza-Castillo D.I., Hernández-Montoya V., Bonilla-Petriciolet A.,Montes-Morán M.A., Synthesis and adsorption properties of activated carbons from biomass of Prunus domestica and Jacaranda mimosifolia for the removal of heavy metals and dyes from water, Industrial Crops and Products, 2013, 42, 315-323.

[66] Vuković G.D., Marinković A.D., Škapin S.D., Ristić M.T., Aleksić R., Perić-Grujić A.A., et al., Removal of lead from water by amino modified multi-walled carbon nanotubes, Chem. Eng. J., 2011, 173, 855-865.

[67] Wang L., Zhang J., Zhao R., Li Y., Li C.,Zhang C., Adsorption of Pb(II) on activated carbon prepared from Polygonum orientale Linn.: Kinetics, isotherms, pH, and ionic strength studies, Bioresour. Technol., 2010, 101, 5808-5814.

[68] Xue Y., Gao B., Yao Y., Inyang M., Zhang M., Zimmerman A.R., et al., Hydrogen peroxide modification enhances the ability of biochar (hydrochar) produced from hydrothermal carbonization of peanut hull to remove aqueous heavy metals: Batch and column tests, Chem. Eng. J., 2012, 200-202, 673-680.

[69] Zaini M.A.A., Okayama R.,Machida M., Adsorption of aqueous metal ions on cattle-manure-compost based activated carbons, J. Hazard. Mater., 2009, 170, 1119-1124.

[70] Zhu H., Jia Y., Wu X.,Wang H., Removal of arsenic from water by supported nano zero-valent iron on activated carbon, J. Hazard. Mater., 2009, 172, 1591-1596.

[71] Zouboulis A.I., Kydros K.A.,Matis K.A., Flotation of powdered activated carbon with adsorbed gold(I)-thiourea complex, Hydrometallurgy, 1994, 36, 39-51.