This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

The Sorption of Arsenic onto Activated Carbon Impregnated with Metallic Silver and Copper

Ljubinka V. Rajaković[a]
[a] FACULTY OF TECHNOLOGY AND METALLURGY, UNIVERSITY OF BELGRADE KARNEGIJEVA 4, BELGRADE, YUGOSLAVIA

To cite this Article Rajaković, Ljubinka V.(1992) 'The Sorption of Arsenic onto Activated Carbon Impregnated with Metallic Silver and Copper', Separation Science and Technology, 27: 11, 1423 — 1433

To link to this Article: DOI: 10.1080/01496399208019434

URL: http://dx.doi.org/10.1080/01496399208019434

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE AND TECHNOLOGY, **27**(11), pp. 1423–1433, 1992

The Sorption of Arsenic onto Activated Carbon Impregnated with Metallic Silver and Copper

LJUBINKA V. RAJAKOVIĆ
FACULTY OF TECHNOLOGY AND METALLURGY
UNIVERSITY OF BELGRADE
KARNEGIJEVA 4, 11 000 BELGRADE, YUGOSLAVIA

Abstract

The adsorption of arsenic species in aqueous solutions onto activated carbon with and without chemical impregnation has been studied. The ability of activated carbon to adsorb arsenic depends on the arsenic oxidation state, the pH of the water, and the activity of the metal used for the activated carbon impregnation. The results of the investigations have shown that physical adsorption is effective only for the arsenic(V) species in water. Activated carbon adsorbs arsenic(V) with a saturation adsorption capacity of 0.27 mmol/g. The chemisorption process is effective for both arsenic species. By impregnation of activated carbon by copper, the sorption process for the arsenic(III) species is significantly improved. The saturation adsorption capacity of the activated carbon impregnated by copper is 0.41 and 0.23 mmol/g for the arsenic(III) and arsenic(V) species, respectively. The pH values of the water are important for both sorption processes because of the change in the ionic forms of both arsenic species. The optimal pH range is between 4 and 9, which is a consequence of the apparent affinity between the carbon surface and arsenic species H_3AsO_3 and $H_2AsO_4^-$ that are predominant at this pH in water. Equilibrium isotherm analyses were undertaken using Langmuir and Freundlich equations.

Key Words: Adsorption; Activated carbon; Impregnation; Water pollution; Equilibrium isotherms; Arsenic; Copper

INTRODUCTION

Activated carbon adsorption is frequently the most efficient and economical method for removing impurities from water, particularly when the impurities are present at low concentrations. It is known that organic compounds adsorb much more strongly onto activated carbon than do inorganic compounds (*1*). Relatively little information is available about the adsorption of specific inorganic compounds by activated carbon. The capacity of activated carbon for a certain type of inorganic pollutant is also important for designing adsorption contacting system. The presence of active metal onto an impregnated activated carbon surface can greatly affect adsorption affinity since some inorganic compounds can be adsorbed preferentially. The aim of the present work is to determine the adsorption capacity of activated carbon for arsenic species in water and to develop the sorption process by introducing a chemisorption function based on adsorption onto activated carbon impregnated by metal.

Arsenic can occur in four oxidation states in water, but in natural waters it is found in only the As(III) and As(V) oxidation states as an anion with acid characteristics (*2*, *3*). The stability and dominance of a certain form depends directly on the pH value of the solution (*4*). In Table 1 the dominant arsenic species depending on pH are presented.

Arsenic compounds are discharged in wastewaters from industries such as pharmaceutical and pesticide manufacturers (*5*) and from mine wastes (*6*, *7*). Arsenic compounds are known to be detrimental to human beings and animals. Arsenic forms both inorganic and organic compounds; the inorganic compounds are more toxic than the organic compounds. The toxicity of arsenic varies greatly according to its oxidation state. Arsenic in the trivalent state is believed to be more toxic than pentavalent arsenic. The toxicity is also dependent on the chemical form, and on the route, duration, and rate of exposure to arsenic. No adverse health effects have been reported from the ingestion of water containing arsenic levels of 1.33×10^{-6} mol/dm^3 (0.1 mg/L) (*2*), but the maximal allowed concentration of arsenic in drinking water is 6.67×10^{-7} mol/dm^3 (0.05 mg/L) (*8*).

EXPERIMENTAL

Materials

All the chemicals used were of analytical grade. Synthetic waters with arsenic concentrations ranging from 1.33×10^{-3} mol/dm^3 (100 mg/L) to

TABLE 1

The Stability and Domination of Arsenic Species in Water as a Function of pH (*12*)

pH	0–9	10–12	13	14
As(III)	H_3AsO_3	$H_2AsO_3^-$	$HAsO_3^{2-}$	AsO_3^{3-}
K	4×10^{-10}	7×10^{-13}	4×10^{-14}	—
pH	0–2	3–6	7–11	12–14
As(V)	H_3AsO_4	$H_2AsO_4^-$	$HAsO_4^{2-}$	AsO_4^{3-}
K	6×10^{-3}	1×10^{-7}	3×10^{-12}	—

1.33×10^{-5} mol/dm^3 (1 mg/L) were prepared by adding a suitable volume of standard arsenic solution to distilled water. The standard solution (arsenic concentration 1.33×10^{-2} mol/dm^3; 1 g/L) was prepared by dissolving the appropriate amount of $NaAsO_2$ or $Na_2HAsO_4 \cdot 7H_2O$ in distilled water with the addition of NaOH which improved the solubility of these salts in water. The pH values of all the solutions used were adjusted with either strong acid (HCl) or strong base (NaOH). The ionic strength of all the water solutions investigated was about 0.001. The adsorbent was coconut granular activated carbon type K-81/B produced by "Miloje Zakić," Kruševac, Yugoslavia. The characteristics and properties of the carbon are listed in Table 2.

Chemical agents (copper and silver) were bonded to activated carbon for chemisorption investigations. For this purpose, solutions of the salts of Ag_2SO_4 and $CuSO_4 \cdot 5H_2O$ were used at concentrations of 0.1 mol/dm^3 with respect to the cations. Impregnation of activated carbon, which has been employed previously (*8*), was accomplished with a standard column chromatography procedure by using the corresponding effluent.

Analysis

Four analytical methods for the determination of arsenic in water were used. The Gutzeit test (standard deviation, ±0.03 mg/L; detection limit, 0.05 mg/L) and the silver-diethyl-dithiocarbamate method (standard deviation, ±0.002 mg/L; detection limit, 0.002 mg/L) were used for arsenic determination in the range of lower concentrations around 0.05 mg/L. The bromatometric and iodometric titration methods (standard deviation, ±0.5 mg/L; detection limit, 1 mg/L) were used in the range of higher concentrations (more than 1 mg/L) (*9*). All tests were carried out in triplicate. An atomic adsorption spectrometer (AAS) Philips SP9 (Cambridge, UK) was used to analyze both the silver and copper content on activated

TABLE 2
Activated Carbon Properties

Ash (%)	5.5
Apparent density (kg/m^3)	440
Iodine number (mg/g)	1200
Pore volume (cm^3/g)	0.9
Surface area BET-N_2 (m^2/g)	1200
Particle size, mean diameter (mm)	0.9
Sieve analysis (DIN 4188)	
	>1.6 mm, 4.5%
	0.425–1.6 mm, 97.5%
	<0.425 mm, 0.5%
	<0.355 mm, 0.2%

carbon and the content of these ions in the water solution after impregnation. In order to confirm the presence of metallic silver and copper on modified carbon surfaces, x-ray analysis was applied by using CuK_α radiation.

Procedure

A continuously mixed bath system was used. Various arsenic concentrations were used. Activated solids were added to a total of 2 dm^3 of arsenic solution (pH 8 and $\mu = 0.001$). Continuous mixing was provided during the experimental period. All solids were aged in the solution for 24 h. The adsorbed amounts were calculated from

$$q_e = \frac{X}{m} = \frac{C_0 - C_e}{m_c}(\text{mmol/g}) \qquad (1)$$

Column Operation. A chromatographic column of 20 i.d. was packed with 11.5 g of each sorbent investigated. An aqueous solution containing 1.33×10^{-3} mol/dm^3 arsenic(III) was passed through the column at room temperature (22°C) at a flow velocity of 0.6 dm^3/h. The effluent was collected in 10 cm^3 fractions, and each fraction was analyzed for arsenic.

RESULTS AND DISCUSSION

In order to investigate the chemisorption process, activated carbon was chemically activated with silver and copper. These metals were chosen because of their reactivity toward arsenic ions in water and the possibility of their forming insoluble compounds (*10*, *11*). After impregnation, activated carbon did not discharge the ions from the surface to the water. The concentrations of copper and silver ions remaining in the water solutions were measured by AAS; they were less than 10^{-6} mol/dm^{-3}. The Auger spectrum of activated carbon impregnated with carbon, presented in Fig. 1, showed that activated carbon is uniformly covered by copper. It also shows that small quantities of chlorine were always present on the surface. This is usually explained as contamination of the carbon surface by the atmosphere.

Three types of activated solids were chosen for the study of the saturation adsorption capacities of arsenic species as shown in Table 3. The amounts of silver and copper bound to active adsorbents were determined by AAS, and they are also given in Table 3.

The data in Table 3 present some important and obvious facts. Arsenic adsorption on activated carbon with or without a chemical agent is an extremely complex process, and it depends on the arsenic valence as well

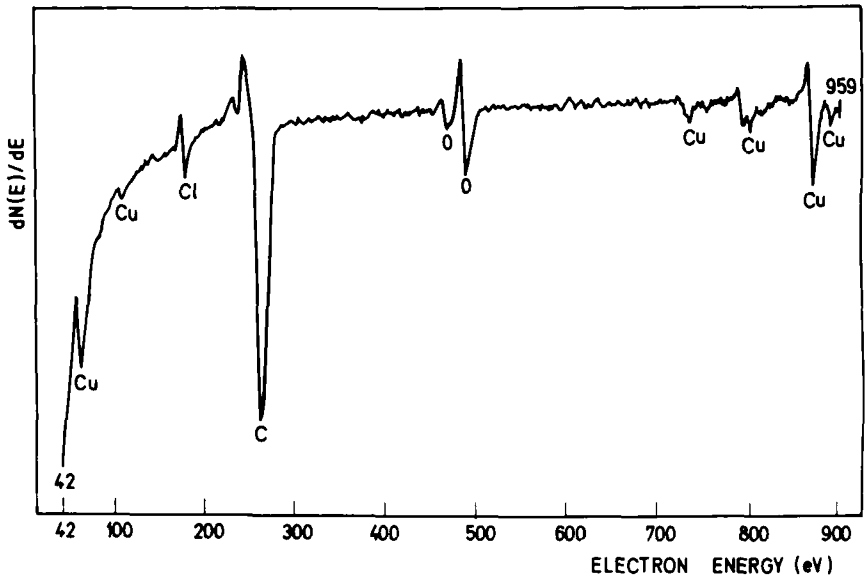

FIG. 1. Auger spectrum of activated carbon impregnated with copper.

as on the pH value of the solution. These results lead to the conclusion that activated carbon adsorbs As(V) better than As(III). The saturation adsorption capacity of the activated carbon for As(V) is 0.27 mmol/g. Activated carbon is inefficient toward As(III). By the chemisorption process onto carbon activated with chemical agents, the removing effect of As(III) was improved: slightly with silver but significantly with copper. The effectiveness of activated carbon was increased from total inactivity to 0.41 mmol/g. It seems that chemical reaction and the formation of the

TABLE 3

Saturation Adsorption Capacities of Activated Carbon for Arsenic Species (pH 8; $\mu = 0.001$; $t = 22°C$)

Active material	Capacity (mmol/g)	
	As(III)	As(V)
Activated carbon	0	0.27
Activated carbon + Ag^+ ions (0.1 mmol Ag^+/g)	0.03	0.03
Activated carbon + Cu^{2+} ions (1.34 mmol Cu^{2+}/g)	0.41	0.23

low solubility precipitate $CuHAsO_3$ on the carbon surface was a favorable process. In the case of As(V), adsorption on impregnated carbon was slightly reduced to 0.23 mmol/g. This can be attributed to partial covering of the free carbon surface with silver and copper during impregnation. In general, physical adsorption is more effective for As(V) while chemisorption is more favorable for As(III). The adsorption process was not notably improved by silver impregnation of activated carbon. For both arsenic species the capacities of activated carbon impregnated by silver were the same: 0.03 mmol/g. The results of this part of investigations indicated the need for further experiments. More detailed investigations used activated carbon impregnated by copper. The effect of pH on arsenic adsorption on activated carbon was studied in the pH range between 2 and 12. The results are shown in Fig. 2.

The data from Fig. 2 clearly indicate that activated carbon is not efficient for the As(III) species in water. It seems that electrostatic interaction is an important mechanism for arsenic adsorption on activated carbon. H_3AsO_3 molecules are the predominant species for As(III) in this pH range, and as neutral molecules they were not adsorbed onto the slightly positive or neutral surfaces of activated carbon. Arsenic(III) is effectively adsorbed only on active carbon impregnated with copper. The optimal pH range was between 8 and 10. In this case the adsorption is preferentially chemisorption, followed by the formation of a low solubility compound, $CuHAsO_3$. Arsenic(V) is effectively adsorbed on both active carbon with and without carbon in the pH range 4 to 9. The anionic forms $H_2AsO_4^-$ and mostly $HAsO_4^{2-}$ are the predominant As(V) species in water in this

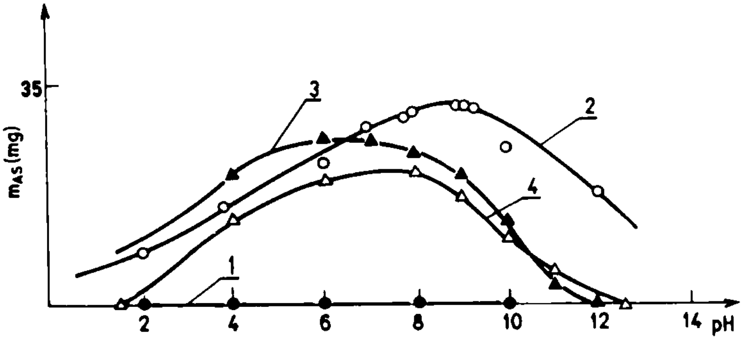

FIG. 2. Effect of pH on the saturation adsorption capacity of activated carbon for As(III) and As(V) in water. (m_{carbon} = 1 g, m_{Cu} = 85 mg, μ = 0.001, t = 15°C.) (1) Arsenic(III)–activated carbon. (2) Arsenic(III)–activated carbon impregnated with copper. (3) Arsenic(V)–activated carbon. (4) Arsenic (V)–activated carbon impregnated with copper.

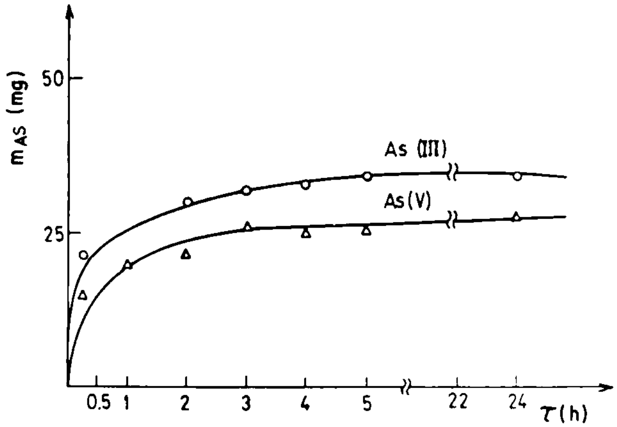

FIG. 3. Kinetics of arsenic adsorption on carbon activated with copper. (C_{As} = 1.33 × 10^{-3} mol/dm^3, m_{carbon} = 1 g, m_{Cu} = 85 mg, pH = 8, μ = 0.001, t = 15°C.)

range. There is an apparent affinity between the carbon surface and the negatively charged arsenic species with oxo-function groups, and they were adsorbed effectively onto the carbon surfaces (*12*, *13*).

The results of the adsorption kinetics of As(III) and As(V) on carbon impregnated by copper are presented in Fig. 3. In both cases the adsorption rate was exponential. Within the first 30 min more than 50% of the arsenic was adsorbed as calculated from the saturation adsorption capacities. As(III) was removed from the solution slightly faster than As(V).

The theoretical isotherms can be obtained from Langmuir and Freundlich equations. Equations (2) and (3) represent the Langmuir and Freundlich equations, respectively.

$$q_e = \frac{q_0 b C_e}{1 + bC_e} \quad \text{(mmol/g)} \tag{2}$$

$$q_e = K_f C_e^n \quad \text{(mmol/g)} \tag{3}$$

Theoretical isotherms for arsenic(V) on activated carbon impregnated with copper were compared with experimental results. They are presented in Fig. 4. The isotherms were obtained at pH 8 in distilled water and μ = 0.001. The best fit was obtained with a Langmuir-type plot, Curve "L" in Fig. 4. The Freundlich plot, Curve "F" in Fig. 4, was found to fit equally well for As(III) and As(V) up to an initial concentration of 6.60 × 10^{-4} mol/dm^{-3} (which corresponds to the equilibrium concentration of 0.5

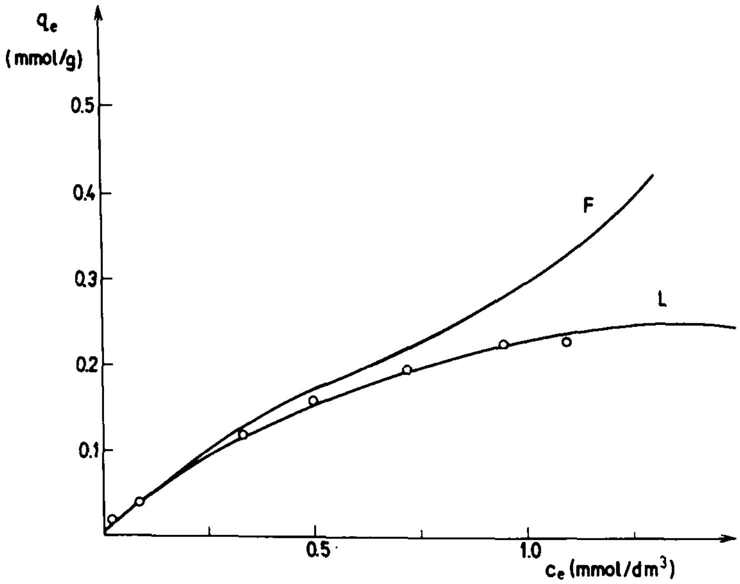

FIG. 4. Comparison of theoretical isotherms for arsenic(V) on activated carbon impregnated with copper. (pH 8, $\mu = 0.001$, $t = 22°C$, $m_{carbon} = 1$ g.) F = Freundlich isotherm; $q_e = 0.1 \times C_e^{0.84}$ (mmol/g); L = Langmuir isotherm; $q_e = \dfrac{5 \times 10^{-4} \times 826 \times C_e}{1 + 826 \times C_e}$ (mmol/g); (○) experimental points.

mmol/dm^3 in Fig. 4). As the isotherms reach saturation and monolayers are formed, the Freundlich plots are not applicable, but up to monolayer formation the "F" plots in Fig. 4 are linear. The Langmuir isotherm gives the best agreement over the whole adsorption range since it predicts the experimentally observed monolayer coverage better than the exponentially increasing Freundlich isotherm. The adsorption isotherms for arsenic(III) and (V) on activated carbon with and without copper are shown in Fig. 5.

The calculated Langmuir parameters for the specified concentration range are listed in Table 4. The theoretically predicted Langmuir monolayer coverages, defined by q_0 in Table 4, are 0.54 mmol/g for arsenic(III) adsorption on activated carbon and 0.40 and 0.36 mmol/g for arsenic(V) on activated carbon and activated carbon impregnated by copper, respectively. The real adsorption capacities, according to the experimentally obtained data presented in Table 3, are close to the theoretical values only for the activated carbon impregnated with copper and arsenic(III). In all cases the residual arsenic concentration in water is less than 6.67×10^{-7} mol/dm^3.

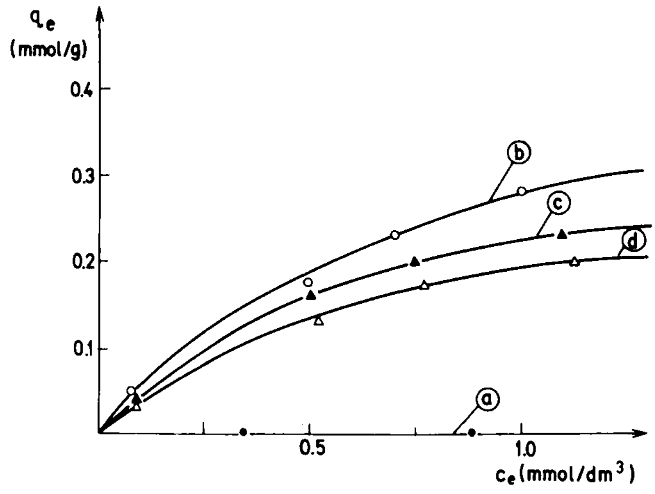

FIG. 5. Langmuir adsorption isotherms of arsenic on activated carbon. (pH 8, μ = 0.001, t = 22°C, m_{carbon} = 1 g, m_{Cu} = 85 mg.) (a) Arsenic(III)-activated carbon. (b) Arsenic (III)-activated carbon impregnated with copper. (c) Arsenic(V)-activated carbon. (d) Arsenic(V)-activated carbon impregnated with copper.

Figure 5 shows the Langmuir isotherm plots for arsenic(III) and arsenic(V) species in the water. The isotherm values were obtained at pH 8 and 22°C. These data also confirmed that activated carbon impregnated by copper exhibits a higher adsorption capacity toward both arsenic species in comparison to activated carbon without chemical impregnation.

Figure 6 shows the breakthrough curves in a column operation using three different sorbents. The best effects in the continuous flow system

TABLE 4

Langmuir Constants for Adsorption of Arsenic Species from Water on Activated Carbon (pH 8; μ = 0.001; t = 22°C)

Parameters	q_0 mol/g	 mg/g	b (dm^3/mol)	Fig. 5 (curve)
As(III):				
Activated carbon	—		—	a
Activated carbon + Cu^{2+}	5. 4 × 10^{-4}	40.5	1250	b
As(V):				
Activated carbon	4. 0 × 10^{-4}	30.0	826	c
Activated carbon + Cu^{2+}	3. 6 × 10^{-4}	27.0	939	d

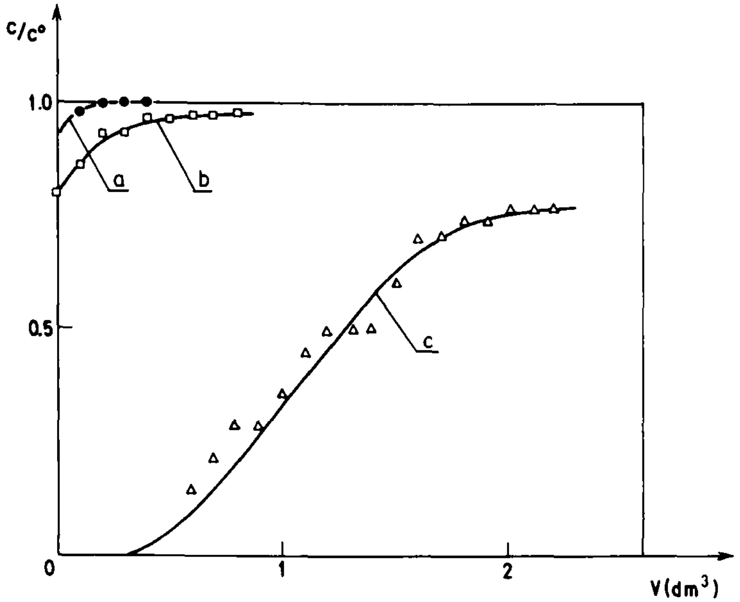

FIG. 6. Breakthrough curves of arsenic(III) in column operation. (pH 8, μ = 0.001, t = 22°C, m_{carbon} = 1 g.) (a) Activated carbon. (b) Activated carbon impregnated with silver. (c) Activated carbon impregnated with copper.

were obtained by activated carbon impregnated with copper. The effectiveness of this sorbent was calculated from the curve in Fig. 6 to be 0.18 mmol/g. It is obvious that the effectiveness of all the sorbents to arsenic bonding and removal was decreased in the flow system (about two times), but this result suggests that the present arsenic adsorption method can be successfully applied to a column-type operation.

CONCLUSION

The adsorption capacity of arsenic species in aqueous solutions onto activated carbon with and without chemical impregnation has been studied. It is concluded that arsenic adsorption can be effectively accomplished by activated carbon impregnated by copper. With this type of sorbent both arsenic species adsorb efficiently from water with saturation capacities of 0.41 (As(III)) and 0.23 (As(V)) mmol/g. Physical adsorption onto activated carbon is a favorable process for arsenic(V) species, while the chemisorption process is favorable for the arsenic(III) species. All the sorption processes are pH dependant. pH values of the water are important because of the change in the ionic forms of both arsenic species. Maximal saturation adsorption capacities are obtained at a pH range between 4 and 9 in water. Activated carbon in this pH range exhibited an apparent affinity toward both arsenic species H_3AsO_3 and $H_2AsO_4^-$ that are predominant in water in this pH range.

NOMENCLATURE

q_e	adsorption density, concentration of arsenic in the carbon at equilibrium (mol/g)
X	quantity of arsenic adsorbed (mol)
m	mass of carbon (g)
m_c	concentration of carbon in solutions (g/dm^3)
C_0	initial concentration of arsenic in solution (mol/dm^3)
C_e	concentration of arsenic in solution at equilibrium (mol/dm^3)
b	Langmuir constant (dm^3/mol)
q_0	maximal adsorption density, concentration of arsenic in the carbon at equilibrium (mol/dm^3)
K_f	Freundlich constant (mol/g)
n	Freundlich exponent

Acknowledgment

Support for this work by the Serbian Research Council is gratefully acknowledged.

REFERENCES

1. W. J. Weber Jr. and J. C. Morris, *J. Sanit. Eng., Div. Am. Soc. Civ. Eng.*, *90*, 79 (1964).
2. Y. F. Ferguson and J. A. Gavis, *Water Res.*, *6*, 1259–1271 (1972).
3. Y. S. Shen, *J. Am. Water Works Assoc.*, *65*, 543–548 (1973).
4. V. S. Pakholkov, S. G. Dvinin, and V. F. Markov, *Zh. Prikl. Khim. Leningrad*, *53*(2), 280–285 (1980).
5. N. L. Nemerow, *Liquid Wastes from Industry—Theories, Practices and Treatment*, Addison-Wesley, Philippines, 1971.
6. W. M. Mok, J. A. Riley, and C. M. Wai, *Water Res.* *22*(6), 769–774 (1988).
7. W. M. Mok and C. M. Wai, *Ibid.*, *23*(1), 7–13 (1989).
8. Lj. V. Rajaković, M. Mitrović, S. Stevanović, and S. Dimitrijević, *Naučno-Tehnički Pregled*, *38*(6), 18–23 (1988).
9. *APHA Standard Methods for the Examination of Water and Wastewater*, 15th ed., Washington, D.C., 1981.
10. C. P. Huang and M. H. Wu, *J. Water Pollut. Control Fed.*, *47*(10), 2437–2446 (1975).
11. Lj. V. Rajaković and M. M. Mitrović, *Environ. Pollut.*, *74*, 310–319 (1991).
12. S. K. Gupta and K. Y. Chen, *J. Water Pollut. Control Fed.*, *50*, 493–506 (1978).
13. Lj. V. Rajaković, Ph.D. Thesis, Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, 1986.

Received by editor September 27, 1991