ORIGINAL PAPER

REMOVAL OF As³⁺ CATIONS FROM WATER BY ACTIVATED CHARCOAL, BENTONITE AND ZEOLITE IN A BATCH SYSTEM AT DIFFERENT pH*

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ABSTRACT

Adsorption of As³⁺ cations by natural materials is a relatively well-studied problem although much remains to be learned about it. As a consequence of pollution, remarkably high arsenic content has been reported in numerous natural waters. The subject of this paper is the adsorption of As³⁺ cations by granulated activated carbon (GAC), bentonite and zeolite (0.1-0.3 g), which could be used prospectively as potential supplement to other materials. The quantitative analysis of all samples was performed by Inductively Coupled Plasma-Optical Emission Spectrometry. The results indicate that the amount of As³⁺ cations in a solution decreases with time for all the three adsorbents. The research also showed that 0.2 g of GAC and bentonite is an optimum adsorbent amount at pH 6.5. The same amount of zeolite has the best adsorption capacity at pH 3.5. Parallel testing of these materials showed that GAC had the highest adsorption potential (50%) compared to bentonite and zeolite (11.7% and 26.5%). Most of the adsorption process by GAC takes place at the first 45 min; in the case of bentonite it is the first 30 min and for zeolites the first 15 min (best starting; 19.5%). The reason for the lower adsorption of As³⁺ cations by bentonite is its instability in acidic environment, while zeolite shows reduced isomorphic replacement ability due to different charges compared to potentially convertible cations. The adsorption of arsenic on these natural materials has proven to be one of the most efficient and economical method of arsenic removal.

Keywords: adsorption, As³⁺, activated charcoal, bentonite, zeolite.

INTRODUCTION

Water toxicity, especially the toxicity of drinking water by arsenic (As), is one of the most acute problems in today's world. Remarkably high arsenic content has been reported in numerous natural waters as a consequence of pollution. In nature, water contamination by arsenic occurs due to the natural erosion and dissolution of rocks that contain arsenic, but also as a result of anthropogenic impact (SHRAIM et al. 1999, BISSEN, FRIMMEL 2003). The concentration range in which arsenic can be found in nature is wide (in natural waters it varies from 0.5 to 5000 mg dm^{-3}, and for rocks the interval is 500 to 2500 mg kg^{-1}). Potable water becomes toxic when the arsenic concentration reaches 2 mg dm^{-3} (HUGHES 2002), thus it is of utmost importance to treat polluted water effectively. A particular problem arises when arsenic is found in low concentrations because arsenic ions are not able to interact with the process material whether adsorption, redox or some different form of filtration processes are applied. Also, a great difficulty in the removing processes arises from an unbalanced relationship between As^{5+} and As^{3+} ions and As ions that are bound to the organic phase (BEDNAR et al. 2004).

According to the classification of the International Agency for Research on Cancer, inorganic trivalent arsenic is classified in group I, which means it is a proven carcinogen for humans, while pentavalent inorganic arsenic and organic arsenic as well as their compounds are classified as toxic substances. The maximum allowed arsenic concentration in drinking water is established at 10 mg dm^{-3} by all regulatory entities, including the World Health Organization and the United States Agency for Environmental Protection (WHO 1996, USEPA 2006).

Various methods and procedures are applied in order to remove arsenic from water. Conventional methods are coagulation and flocculation, precipitation, adsorption, ion exchange and membrane filtration (WANG et al. 2004). Alternative methods such as ozone oxidation, bioremediation and electrochemical treatment are also used, but these methods require detailed research before their wider application in systems for arsenic removal. The adsorption of arsenic on natural materials is one of the most efficient and economical methods of arsenic removal. Natural mineral materials such as GAC, bentonite and zeolites, owing to good adsorptive properties and prices, are usually used in the removing processes of many harmful agents, including toxic arsenic.

According to the recommendations of USEPA, adsorption on GAC is one of the best available technologies used for removing many substances from water (JACANGELO et al. 1995), as well as to control the formation of disinfection by-products (USEPA 1999*a*). GAC is a good adsorbent for the removal of dissolved industrial chemicals, heavy metals and arsenic from water, but not better than powdered activated carbon (NEWCOMBE 1994, ANSARI, SAGEDH 2007). The functional groups on its surface endow it with an amphoteric

character. Depending on the solution pH value and the nature of an adsorbate, the adsorption mechanism may be based on dipole-dipole interactions, hydrogen or covalent bonding, or ion exchange (CHINGOMBE et al. 2006).

The dominant mineral in bentonite is montmorillonite (a mineral from the spectate group), which makes >70% of its composition. In addition to this mineral, there are usually plagioclase, illite and zeolite. In montmorillonite, layers consisting of $[SiO_4]$-tetrahedrons enclose layers of octahedral compounds with the formula $[M(O_5, OH)]$, where M is usually Al or Mg, but Fe is also often found. The silicate layers have a small negative charge that is compensated by exchangeable ions in the intercrystallite region. The charge is so weak that the cations (in natural bentonite, predominantly Ca^{2+}, Mg^{2+} or Na^+ ions) can be adsorbed in this region with their hydrate shells (MEUNIER 1998).

In addition to GAC and bentonite, zeolites are also effective adsorbents and ion exchangers for metal ions (MORENO et al. 2001), and adsorption, as with clay and GAC, is conditioned by a number of factors. The crystal structure of zeolite, which looks like a sponge with holes of different diameters, can absorb different compounds.

Arsenic adsorption on natural materials in different experimental conditions in order to remove arsenic from water down to the legally accepted values is the subject of this paper. Selected natural materials that have been tested are GAC, bentonite clay and zeolite. The conclusions about their potential use are given on the basis of the laboratory results obtained.

MATERIAL AND METHODS

Adsorbents

GAC having a 2 mm particle size was supplied by the plant Miloje Zakić-Kruševac. Bentonite originated from Prisjan (Serbia). The chemical composition of dried bentonite clay at 110°C was: 51.8% SiO_2, 0.3% TiO_2, 26.9% Al_2O_3, 2.3% Fe_2O_3, 0.1% MnO, 1.3% MgO, 1.4% CaO, 0.8% Na_2O and 2.1% K_2O (STOJILJKOVIĆ et al. 2015). Samples of natural zeolites were supplied by the plant MineraliCO-Vranjska Banja and prepared by grinding up to 100% of particles of the 2 mm size at the Vranje Spa facility. The chemical composition of zeolite was: 64.7% SiO2, 13.1% Al2O3, 3.5% Fe_2O, 5.2% CaO, 0.8% MgO, 1.2% Na_2O and 1.1% K_2O (STOJILJKOVIĆ et al. 2014).

Standard solution preparation

Merck standard solution which contained As^{3*} cations (sodium arsenite standard) at the concentration of 1000 mg dm^{-3} was used for the preparation of calibration solutions. Arsenic standard solutions were prepared from calibrated solutions so that concentrations of the standard for the calibration

chart were in the range of expected element concentrations. Distilled water purified by Fisher Chemical (HPLC grade) was used for dilution of samples. The final concentration of arsenic was adjusted to 2 mg dm^{-3}. The contact time was 120 min under normal conditions. The contact time between standard solution-adsorbent (GAC, bentonite and zeolite) systems was in the range 0-120 min.

Sampling and sample preparation

Arsenic solution (at a concentration of 2 mg dm^{-3} and pH 3.5, 6.5, 8.5 & 10) in a volume of 100 cm^3 distilled water was stirred with a magnetic stirrer along with the predetermined amount of an adsorbent. Water samples were taken at specified time intervals (0, 5, 15, 30, 45, 60, 90 and 120 min) and then filtered under vacuum through a 0.1 µ diameter filter. After that, the samples were subjected to ICP-OES analysis.

Inductively Coupled Plasma-Optical Emission Spectrometry

Arsenic in the water fraction was analyzed by ICP-OES Spectro-Arcos (1.4 kW; 12 MHz). The ICP-OES analysis was performed by measuring the intensity of radiation of specific wavelengths emitted by As. The samples were dispersed in liquid and introduced into the plasma in the form of aerosol, where they were vapourized, atomized and excited. The carrier gas was Argon 5.0 (99.999% purity). Total uncertainty (including accuracy error) of the analysis is less than 2%.

RESULTS AND DISCUSSION

Chemistry

Arsenic might be unique among the heavy metalloids and oxyanion-forming elements and its sensitivity to mobilization at pH values typically found in groundwater (pH 6.5-8.5) and under oxidizing and reducing conditions as oxyanions of As^{3+} or As^{5+} (HEM 1985). The pH of a solution determines the chemistry and speciation of arsenic ions and also affects the surface charge of the adsorbent. Under oxidizing conditions and at low pH, H$_2$AsO$_4^-$ is dominant (less than about pH 6.9), whilst HAsO$_4^{2-}$ becomes dominant at higher pH (H$_3$AsO$_4$ and AsO$_4^{3-}$ may be present in extremely acidic and alkaline conditions respectively). Under reducing conditions and at pH less than about 9.2, uncharged arsenite species will predominate (BROOKINS 1988) – Figure 1.

The most common forms of arsenic in which it occurs are arsenous acid, arsenic acid, oxy thiorsenate acid, monomethylarsenate acid, dimethylarsenate acid, dimethylarsenite acid, threemethylarsine, threemethylarsine oxide, monomethylarsenate acid, arsenocholine and arsenobetaine (NING 2002,

ZOUBOULIS, KATSOYIANNIS 2002). Since arsenic is a redox-sensitive element, its distribution in the natural environment is influenced by many factors, such as pH of the environment, oxidation-reduction reaction, distribution of other ion forms, chemical and microbiological properties of the aqueous medium (SHIH 2005). In surface water, where oxidative conditions prevail because of the constant contact with air oxygen, the dominant equilibrium form is pentavalent arsenic, As^{5+}:

$$H_3AsO_4 \leftrightarrow H^+ + H_2AsO_4^- \leftrightarrow 2H^+ + HAsO_4^{2-} \leftrightarrow 3H^+ + As_4^{3-} \qquad (1)$$

while under moderate reduction conditions, the equilibrium form of trivalent arsenic, As^{3+} dominates:

$$H_3AsO_3 \leftrightarrow H^+ + H_2AsO_3^- \leftrightarrow 2H^+ + HAsO_3^{2-} \leftrightarrow 3H^+ + AsO_3^{3-} \qquad (2)$$
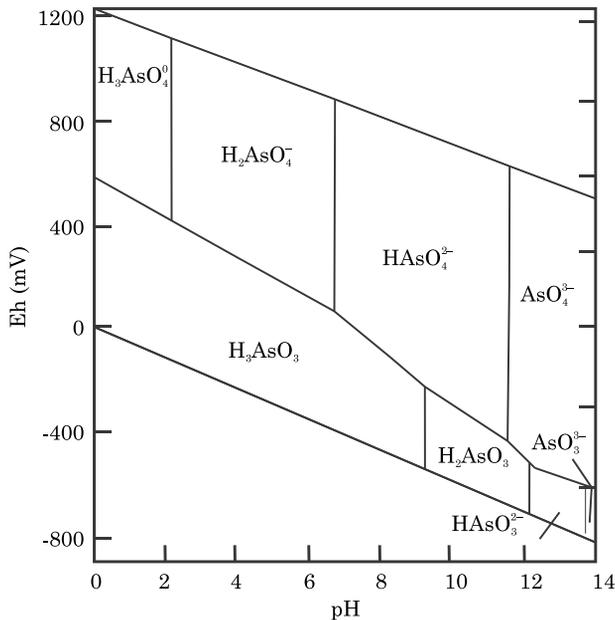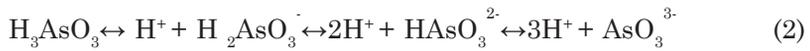

Fig. 1. Eh–pH diagram for aqueous arsenic species at 25°C and total pressure of 1 bar (BROOKINS 1988)

Research in a batch system and the influence of pH on adsorption

Research on the adsorption of As^{3+} cations in a batch system demonstrated the adsorptive activity of GAC, bentonite and zeolite, which varied at different pH values. Figure 2 shows the adsorption results at a pH optimum for GAC (6.5), bentonite (6.5) and zeolite (3.5). The juxtaposition of the results implicates that the optimal weight for all samples is 0.2 g.
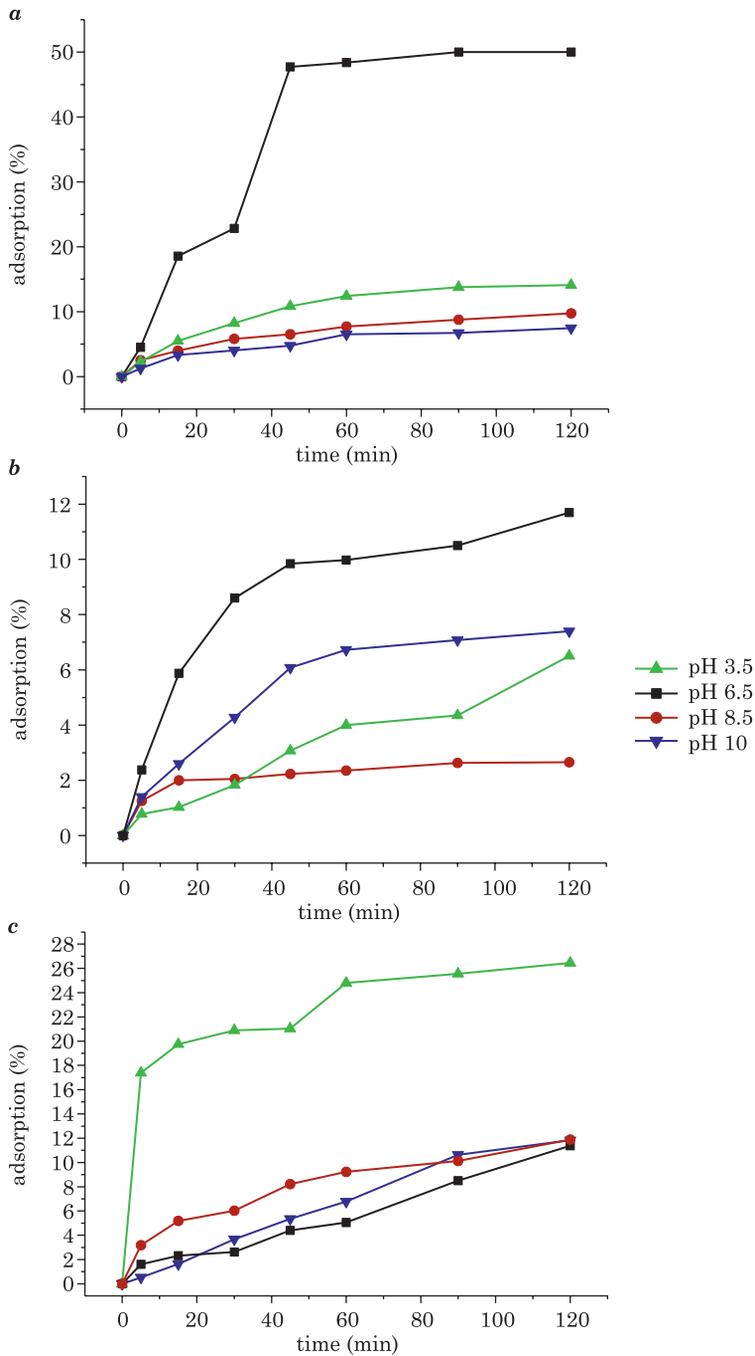
Fig. 2. Adsorption of As³⁺ cations in a batch system by GAC (*a*), bentonite (*b*) and zeolite (*c*) with the mass of a sample of 0.2 g and different pH

In the adsorption process of As^{3+} by GAC, two phases can be observed: the first phase from 0-45 min, when the adsorption peaks at 47.8%, and the second one from 45-120 min, when the adsorbent becomes saturated (after 90 min) (Figure 2*a*). The adsorption of cations on GAC after 120 min was 50%. Based on the results at pH 6.5 for bentonite, an overall degree of adsorption was 11.7% (Figures 2*a* and 3). From Figure 2*b* and Figure 3, it can be inferred that most of the adsorption (8.6%) occurs in the period of 0-30 min, while less adsorption (3.1%) takes place in the 30-120 min period. In contrast to GAC and bentonite, zeolite performed the best during initial adsorption as the largest amount of A_S^{3+} cations was adsorbed in the first 15 min of adsorption (19.5% of the total 26.5 %) – Figure 2*c*.
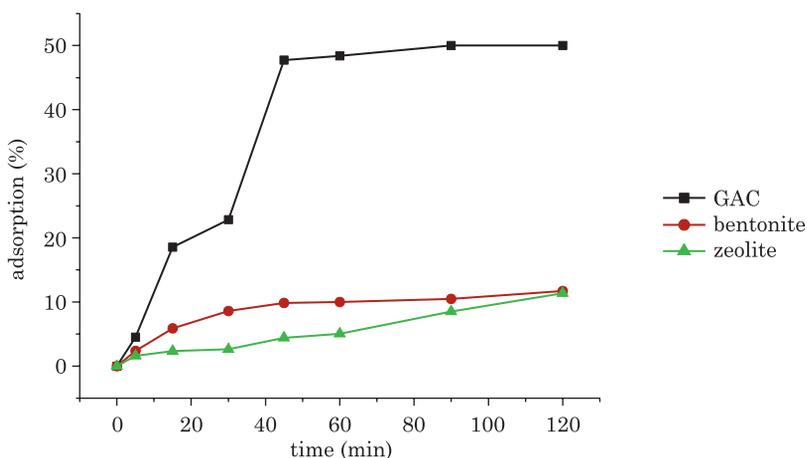

Fig. 3. Adsorption of As^{3+} cations in a batch system by GAC, bentonite and zeolite under mass of 0.1 g and pH 6.5

By analogy to the previous experiment, the adsorption capacity of the three adsorbents at pH 6.5 (Figure 4) with the sample masses of 0.1, 0.2 and 0.3 g was compared. The results showed the highest degree of adsorption when the weight of a sample was 0.2 g in the case of GAC and bentonite and 0.1 g for zeolite.

The efficiency of As^{3+} cations binding

The results showed that GAC has better As^{3+} binding efficiency (50%) compared to bentonite (11.7%) and zeolite (26.5%). GAC possesses a very large specific surface area (>500 m^2 g^{-1}; by many authors), well-developed porosity and tunable surface-containing functional groups (BAKER et al. 1992, ZONGXUAN et al. 2003), imparting the material with important adsorptive properties. Adsorption on GAC mostly takes place on the surface of pores.
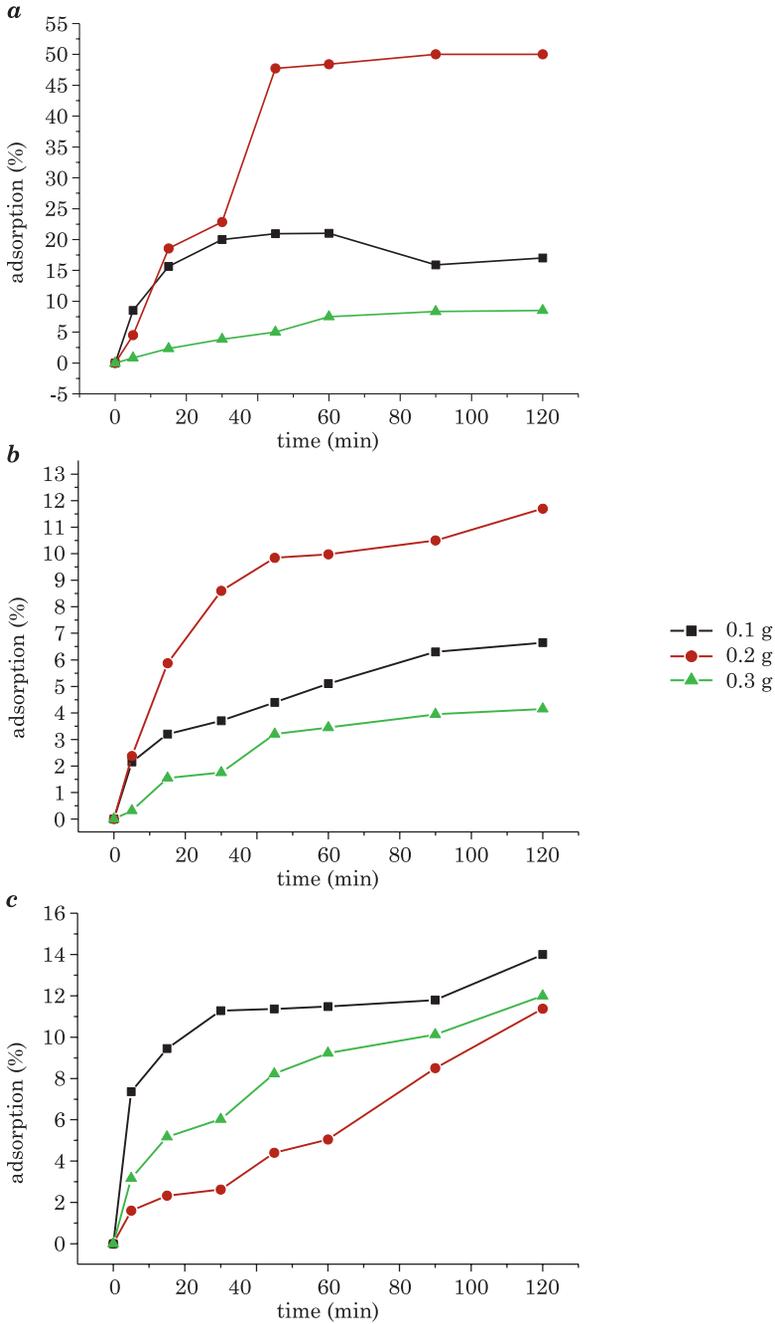
Fig. 4. Adsorption of As^{3+} cations at pH 6.5 in relation
to the various weights of GAC (*a*), bentonite (*b*) and zeolite (*c*) samples

Based on these facts, it can be justified to claim that a higher degree of arsenic removal can be obtained when the adsorbent mass in a batch system is 0.2 g than when the weight of a GAC sample is 0.1 g. However, a system with an adsorbent mass of 0.3 g did not achieve the greatest efficiency. This result can be explained by the fact that adsorption is not only dependent on the weight of an adsorbent, but also on the number of available pores which are located on the adsorbent (Li et al. 2002).

Montmorillonite produced from bentonite possesses a large specific surface area ($6\text{-}8 \cdot 105$ m^2 kg^{-1}) and a relatively high structural charge (up to 1200 meq kg^{-1}), imparting the material with important adsorptive properties (Premović et al. 2008). Based on these parameters, we could expect better adsorption properties compared to GAC; however, the results did not verify it. The stability of montmorillonite mineral lattices depends on the ability of various ions in the environment either to remain in an equilibrium with the clay mineral or to replace exchangeable ions. Namely, this mineral is stable in a neutral to slightly alkaline medium (pH $\geq$ 7) and is unstable under highly acidic conditions (pH $\leq$ 6) and in alkaline environments (pH $\geq$ 8). Under acidic and basic conditions, H$^+$ and OH$^-$ ions can replace metal cations in the structure of montmorillonite, making this mineral unstable (Premović et al. 2008).

Zeolite reaches the maximum degree of adsorption at pH 3.5 and with a mass of 0.2 g. The reason probably lies in the fact that the adsorption of As^{3+} cations largely depends on protonation which dominates at certain pH values on the surface of aluminum groups and on the oxidation state of arsenic (Shevade, Ford 2004). The lower adsorption of As^{3+} cations by zeoliote compared to GAC can be explained by different electric charges of ions and potentially replaceable Na$^+$, K$^+$, Ca^{2+}, Mg^{2+}.

CONCLUSION

The results indicate that the amount of As^{3+} cations in a solution with each of the three adsorbents decreases over time. The optimum mass of all the tested adsorbents is 0.2 g. The most suitable pH value for GAC and bentonite is 6.5.

GAC achieves the maximum adsorption value (50%). The highest quantity of As^{3+} cations is adsorbed during the first 45 min (47.8%) and saturation occurs after 90 min.

Bentonite has the lowest adsorption value (11.7%). For this mineral, most of the adsorption (8.6%) occurs in the period of 0-30 min, while less adsorption (3.1%) takes place in the period of 30-120 min. The main reason for the low adsorption on GAC is the instability of this mineral in acid and basic media.

In contrast to GAC and bentonite, a dose of 0.2 g of zeolite showed the best adsorption properties at pH of 3.5 (26.5%). The best adsorption on zeolite is obtained at pH 6.5 and with the weight of a dose equal 0.1 g. At pH 6.5, the mineral performed the best in terms of the initial adsorption. Namely, the largest percentage of As^{3+} cations was adsorbed in the first 15 min (19.5%). Different electric charges of the tested and potentially interchangeable cations caused lower adsorption by GAC.

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