

Adsorption of cesium on different types of activated carbon

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1 Introduction

Cs-137 ($T_{1/2} \approx 30$ years) is an important long-term contributor to environmental contamination. It is released into the biosphere by nuclear weapons testing or reactor accidents [1]. For example, the release by the accident at the Fukushima Daiichi nuclear power plant raised the Cs-137 concentrations in the local groundwater to concentrations above the drinking water limit in downstream areas like the Fukushima port [2]. Cs salts are very soluble in water, but strongly bind to soils and minerals (Public Health Service, 2004). These properties are used to investigate the removal of Cs from water using a wide range of low-cost adsorbents [3].

In order to remove (radio-)caesium from water, adsorption on activated carbon (AC) is suggested as an economical and straightforward method to concentrate low levels of Cs on a compact adsorbent. Considering the high pH point of zero charge of several ACs, adsorption should be performed at high pH [4]. The goal of this work is to determine the best adsorption conditions for removal of low levels of Cs from radioactive wastewater, using AC. In this research, ACs from brewer's spent grain (BSG) are compared to two commercially available industrial ACs. The BSG AC's are produced in a tube reactor using steam activation [5].

2 Experimental

2.1. Methods and materials

A 1000 ppm Cs ($\sigma = 29$ barn) standard solution (VWR CertiPur, traceable to NIST) was irradiated in the neutron flux of the BR-1 reactor at SCK-CEN Mol to obtain a Cs-134 solution. From the mother solution, three dilutions with different pH (7, 10 and 12) were prepared, adjusting the pH with ammonia. Dilution factors and concentrations were calculated by measuring the samples in a NaI well detector (nearly 100% efficiency for Cs-134) and in an ionisation chamber. Cs-134 serves as a tracer for the total amount of Cs in the solution and its activity can be correlated to the concentration.

Adsorption experiments are carried out at 3 different pH's using 10 different ACs: 2 commercially available AC's (Norit G1240, Filtrasorb F400), 3 AC's from BSG, and the same 5 AC's previously loaded with a small amount (0,5 %) of Prussian Blue (PB) prior to the adsorption experiment in order to further enhance Cs adsorption. The amount of PB on the AC's is determined by calculating the difference between the iron concentrations (measured via ICP-AES) of a PB solution before and after adsorption of PB on AC. Approximately 25-30 mg of AC is put into contact with 9 g of the active Cs solution (± 1.2 ppm Cs; 0.6 Bq/g) and the total activity is determined by measuring the tubes in the NaI well. These tubes are shaken for 36 hours. The solution is filtered using plastic funnels and Whatman ashless filters to separate the AC from the solution. The emptied tubes, the filters with AC and the tubes with the collected solutions are measured in the NaI well. From the measurement, the fraction of Cs-134 adsorbed on the AC and the fraction remaining in the solution are calculated. For the column experiments, Bio-rad Poly-Prep Chromatography Columns (0.8 x 4 cm) (Bio-Rad, California, USA) were filled with approximately 0.7 g of Norit GAC 1240 and pre-wetted with water. 11 mL of approximately 37 Bq g⁻¹ ¹³⁴Cs solution at pH 4, 7, 10 and 12 was poured over these columns and collected, by gravity, in a centrifuge tube. The activity of the collected solution, as well as the activity remaining in the empty centrifuge tube, were both measured in the well-type detector. The collected solution was then poured over the column again. This cycle was repeated five times.

2.2 Results

Properties of the adsorption behaviour of Cs are displayed in **Table 1**. Both the activity concentration and Cs concentration are displayed before and after adsorption from a solution with different pH, averaged for the three ACs. The removal percentage is also calculated. Adsorption is limited at each pH, but the highest removal percentage is reached at a pH of 10. Higher pH leads to competition with ammonia.

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pH	Activity concentration before adsorption (Bq g ⁻¹)	Cs concentration before adsorption (mg L ⁻¹)	Activity concentration after adsorption (Bq g ⁻¹)	Cs concentration after adsorption (mg L ⁻¹)	Removal percentage
7	59.2 ± 0.7	1.16 ± 0.01	48.6 ± 1.9	0.95 ± 0.04	18 ± 3
10	59.7 ± 0.7	1.17 ± 0.01	47.1 ± 1.3	0.93 ± 0.02	21 ± 2
12	60.4 ± 0.7	1.19 ± 0.01	49.2 ± 1.2	0.96 ± 0.02	19 ± 1

Table 1: Average Cs concentration in adsorption solutions and on AC surface of experiments at 3 pHs.

Fig. 1 displays the influence of pH on the adsorption capacity for Norit GAC1240 after a number of filtration cycles using 1 column. The competition effect with ammonia limits the adsorption capacity at high pH, washing away the Cs from the AC. At neutral or slightly acidic pH, the adsorption capacity reached its maximum after approximately 3 to 4 cycles.

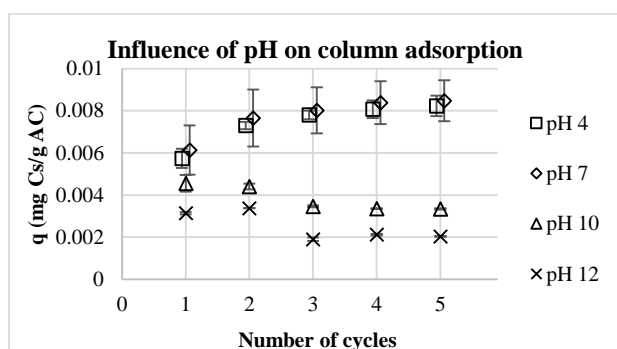


Fig.1. Influence of solution pH on the adsorption capacity of a Norit GAC1240 column after several uses.

3 Conclusions

Batch experiments using a variety of ACs adsorbing Cs from solutions with different pH showed no significant difference between the adsorption capacities at equilibrium for Cs (expressed as q_e values in mg Cs per gram AC) on either commercial AC or AC from BSG. Also the difference in adsorption between the Cs solutions of different pH was not significant. Binding PB on the ACs prior to the adsorption of Cs showed no significant effect on the q_e for any of ACs.

A column experiment with Norit GAC 1240 using 4 solutions with a different pH showed that a neutral to slightly acidic pH increased the adsorption of Cs. At a higher pH the effect of the competition with ammonia ions caused a decrease of q_e .

References

- Whicker, F.W., et al., *Cesium-137 in the Environment: Radioecology and Approaches to Assessment and Management*, in *NCRP Book No. 154 National Council on Radiation Protection and Measurements*. 2007, Bethesda.
- TEPCO, *Detailed analysis results in the port, discharge channel and bank protection at Fukushima Daiichi NPS (As of August 28)*. 2013.
- Li, D., et al., *Aqueous 99Tc, 129I and 137Cs removal from contaminated groundwater and*

sediments using highly effective low-cost sorbents. *Journal of Environmental Radioactivity*, 2014. **136**(0): p. 56-63.

- Hanafi, A., *Adsorption of cesium, thallium, strontium and cobalt radionuclides using activated carbon* *Journal of Atomic and Molecular Sciences*, 2010. **1**(4): p. 292-300.
- Vanreppelen, K., et al., *Activated carbon from pyrolysis of brewer's spent grain: Production and adsorption properties*. *Waste Management & Research*, 2014.