# Capture of aqueous radioiodine species by metalated adsorbents and applications for the nuclear industry: a mini review

Thomas J. Robshaw, Joshua Turner, Sarah Kearney, Brant Walkley, Clint A. Sharrad & Mark D. Ogden

**Table S1.** Comparison of properties of all metalated adsorbents discussed in the review for aqueous iodine adsorption.

| Line | Adsorbent matrix | Loading metal | Synthesis | BET surface area ($m^2$ $g^{-1}$) | Metal loading achieved (mg $g^{-1}$) (mmol $g^{-1}$) | Iodine capacity (mg $g^{-1}$) (mmol $g^{-1}$) | Iodine species targeted | Iodine concentration in solution (mg $L^{-1}$) | Adsorbent mass per L solution in static studies (g) | Relevant conditions/ co-contaminants | Determination of capacity | Time taken for adsorption equilibrium | Flowrate for dynamic experiments (mL $hr^{-1}$) | Leaching test on iodine-loaded material | Notes | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Activated carbon | Ag | Commercially available | 1193 | 11<br>0.097 | N/A | Iodide | 0.6-6 | 10 | Simulated Hanford low activity aqueous waste. ~8 M Na | N/A | <2 days | N/A | Water (~1 mg $g^{-1}$ Ag leached) and 7.8 M NaOH (minimal leaching) | Distribution coefficient, rather than maximum uptake was measured (5.8 x $10^6$) | Asmussen *et al.* [1] |
| 2 | Activated carbon | Ag | Ag-doped form commercially available. Treated with HCl to produce AgCl-loaded form | 802 | 8.7<br>0.081 | 13<br>0.10 | iodide | 1.27 x $10^{-6}$-1.27 | 0.4 | Contaminated ground water. High nitrate (>1000 mg $L^{-1}$) | Estimated from isotherm (not modelled) | 3 days | Not stated | Mild acid (pH 4.5) and base (pH 9) Ag leaching was <0.1% of total mass | 10% of the loaded Ag bled from column experiments at pH 4.5 | Karanfil *et al.* [2] |
| 3 | Activated carbon | Cu | Solvothermal: polyamine loaded with Cu(II) ions and heated in autoclave with activated carbon | N/A | 170<br>2.7 | 41<br>0.32 | iodide | 1-30 | 0.2-8 | Chloride and sulfate (200 mg $L^{-1}$). 10-15% reduction in performance | Isotherm (Langmuir model) | ~60 min (90% within 20 min) | N/A | Mild acid (pH 5) and base (pH 9) up to 6% iodide leached | | Zhang *et al.* [3] |
| 4 | TrisKem International CL resin / non-functionalised XAD-4 resin (3:4 ratio) | Ag | Immersion of resin in $Ag^+$ solution | N/A | 7.5<br>0.070 | 25<br>0.20 | Not defined | N/A (activity measurements were used) | N/A | 1 M nitric acid (molybdate removed by alumina pre-column) | I-131 activity in column effluent | 2.5 hr (~90% within 30 mins) | 5400-11200 | N/A | Functionality not disclosed but is selective for PGMs. Described as an "extraction chromatography" resin, so likely solvent-impregnated | Decamp and Happel [4] |

| Line | Adsorbent matrix | Loading metal | Synthesis | BET surface area ($m^2$ $g^{-1}$) | Metal loading achieved (mg $g^{-1}$) (mmol $g^{-1}$) | Iodine capacity (mg $g^{-1}$) (mmol $g^{-1}$) | Iodine species targeted | Iodine concentration in solution (mg $L^{-1}$) | Mass of adsorbent used per L solution in static studies (g) | Relevant conditions/ co-contaminants | Determination of capacity | Time taken for adsorption equilibrium | Flowrate for dynamic experiments (mL $hr^{-1}$) | Leaching test on iodine-loaded material | Notes | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 5 | Bispicolylamine ion-exchange resin | Cu | Contact with $CuCl_2$ solution | N/A | 80<br>1.3 | 300-450<br>2.4-3.5 | iodide and iodine | 50-2000 | 2 | pH 0-13, 10:1 molar ratios of nitrate and molybdate (55% reduction in performance) | Isotherm (Langmuir / Dubinin-Radushkevich model) | N/A | 5.5 | N/A | $Cu^{2+}$ was reduced to $Cu^{+}$ in-situ, causing formation of $I_3^-$ | Robshaw *et al.* [5] |
| 6 | Synthetic zeolite derived from coal fly ash | Ag | Activation with NaOH, then contact with aqueous $Ag^+$ to cause cation-exchange, then reduction to Ag(0) claimed | 34-51 | 20<br>0.19 | 20<br>0.16 | iodide | 75-450 | 5 | Chloride, carbonate, bromide and chromate (300 mg $L^{-1}$). Negligible reduction in performance | Estimated from isotherm (not modelled) | >10 days | N/A | HCl (pH 2.5) and water. 1.4% iodine leached | The adsorbent had to be kept in the dark prior to use, to prevent oxidation of Ag nanoparticles. | Tauanov and Inglezakis, [6] |
| 7 | Zeolite | Ag | Commercially available | 310 | 350<br>3.2 | N/A | Iodide | 0.6-6 | 10 | Simulated Hanford low activity aqueous waste. ~8 M Na | - | <1 day | N/A | Water (~40 mg $g^{-1}$ Ag leached) and 7.8 M NaOH (~20 mg $g^{-1}$ Ag leached) | Distribution coefficient, rather than maximum uptake was measured (4.1 x $10^5$) | Asmussen *et al.* [1] |
| 8 | Titanate | Ag | Reaction of Ti salt with NaOH in autoclave, then contact with aqueous $Ag^+$, causing exchange of $Na^+$, then $Ag_2O$ precipitation | 157 | 410<br>3.8 | 430<br>3.4 | Iodide | 100-1100 | 1 | Chloride only (100:1 molar ratio contaminant:iodide). No effect on performance | Estimated from isotherm (not modelled) | 1 hr (adsorption is much faster in high chloride concentrations) | 24-72 | 0.1 M NaCl. Minimal leaching | | Bo *et al.* [7] |
| 9 | Titanate | Ag | Treatment of $TiO_2$ with $AgNO_3$ under UV light. Exchange of $Na^+$, then $Ag_2O$ precipitation | 154 | 60<br>0.56 | 210<br>1.7 | iodide | ≤1400 (estimated from isotherm) | 1 | Very high chloride only (130 g $L^{-1}$, causing 10% decrease in iodide uptake) | Isotherm (Langmuir model) | 6 hr | N/A | N/A | Used visible light for photocatalytic reduction of Ag(0) to $Ag^+$, activating the adsorbent for iodide capture. Adsorbed species was a silver polyiodide complex (desorbed at 350°C) | Liu *et al.* [8] |
| 10 | Silica aerogel | Ag | Aerogel functionalised with mercapto-silanes, contacted with $Ag^+$. reduced to Ag(0) with $H_2$ | 85 | 360<br>3.3 | 88<br>0.69 (iodide) | Iodide and iodate | 5.6-7 (iodide only) | 10 | Simulated Hanford site waste (off-gas condensate simulant). 4580 mg $L^{-1}$ nitrate, 1450 mg $L^{-1}$ fluoride and 2340 mg $L^{-1}$ sulfate | single batch experiment at extremely high [I·] (17 g $L^{-1}$) | 1 hr in deionised water. ~2 days in simulated off-gas condensate | N/A | N/A | Iodate removal mechanism was by reduction to iodide (forming AgI) | Asmussen *et al.* [9] |
| 11 | Argentite | Ag | Precipitation from addition of $AgNO_3$ to $Na_2S$ | 1.1 | 900<br>8.3 | N/A | Iodide | 0.6-6 | 10 | Simulated Hanford low activity aqueous waste. ~8 M Na | - | ~15 days | N/A | Water (~2 mg $g^{-1}$ Ag leached) and 7.8 M NaOH (minimal leaching) | Distribution coefficient, rather than maximum uptake was measured (2.5 x $10^5$) | Asmussen *et al.* [1] |

| Line | Adsorbent matrix | Loading metal | Synthesis | BET surface area ($m^2$ $g^{-1}$) | Metal loading achieved (mg $g^{-1}$) (mmol $g^{-1}$) | Iodine capacity (mg $g^{-1}$) (mmol $g^{-1}$) | Iodine species targeted | Iodine concentration in solution (mg $L^{-1}$) | Mass of adsorbent used per L solution in static studies (g) | Relevant conditions/ co-contaminants | Determination of capacity | Time taken for adsorption equilibrium | Flowrate for dynamic experiments (mL $hr^{-1}$) | Leaching test on iodine-loaded material | Notes | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12 | $Mg(OH)_2$ | Ag | Mixing of MgO and $AgNO_3$ in water | 78 | 350<br>3.2 | 370<br>2.9 | iodide | 0.5-800 (estimated from isotherm) | 1 | Chloride, sulfate, nitrate and carbonate (100:1 molar ratio contaminant:iodide). Minimal reduction in performance | Estimated from isotherm (not modelled) | <20 min | N/A | Mild acid (pH 3) and water. Minimal leaching | | Chen *et al.* [10] |
| 13 | $Cu_2O$ | Ag | Reduction of $CuSO_4$, with incorporation Ag(0) sol | N/A | 10<br>0.093<br>(Ag only) | 26<br>0.20 | iodide | 2.5-25 | 1 | Chloride, sulfate, nitrate and carbonate (10:1 molar ratio contaminant:iodide). Carbonate caused 20% reduction in performance | Estimated from isotherm | 1 hr | N/A | N/A | Superior performance in the absence of visible light, due to photocatalytic activity | Mao *et al.* [11] |
| 14 | Bismuth oxide powder | Bi | Solvothermal: $Bi(NO_3)_3$ dissolved in ethylene glycol/ethanol and heated in autoclave | N/A | 920<br>4.4 | 290<br>2.2 (iodide)<br>230<br>1.3 (iodate) | Iodide and iodate | 0.5-700 | 0.2 | Synthetic seawater and individual competing anions (20 g $L^{-1}$). Chloride and carbonate caused large reduction (75%) in performance | Isotherm (Langmuir model) | ~90 min (90% within 20 min) | N/A | Water. 2.3% loaded iodide leached | | Liu *et al.* [12] |
| 15 | Mineral (copper carbonates malachite and azurite) | Cu | Mixing with powdered Cu(0) | 0.18-0.33 | Not calculated | Not calculated | Iodide only | 1270-12700 | 93 | Deionised water only | N/A | ~4 days | N/A | N/A | | Lefevre *et al.* [13] |
| 16 | $Cu_2O$ | Cu | hydrothermal reduction of $Cu(NO_3)_2$ by formic acid in water/ethanol with ammonia | N/A | 800<br>13 | 23<br>0.18 | iodide only | 2.5-38 | 1 | pH 3-10 (ineffective at higher pH). 100:1 molar ratios of chloride (~30% performance reduction), carbonate (~60% reduction), sulfate and nitrate (minimal reduction) | Isotherm (Langmuir model) | ~ 6hr | N/A | N/A | | Mao *et al.* [14] |
| 17 | Mineral ($BiPbO_2(NO_3)$) | Pb/Bi | Solid-state heating of Pb and Bi salts | N/A | Not calculated | Not calculated | iodide | 150 | 200 | pH 14, carbonate, nitrite and nitrate with total concentration ~400 g $L^{-1}$ (caustic scrubbing solution simulation) | N/A | 10 hr | N/A | N/A | | Kodama [15] |

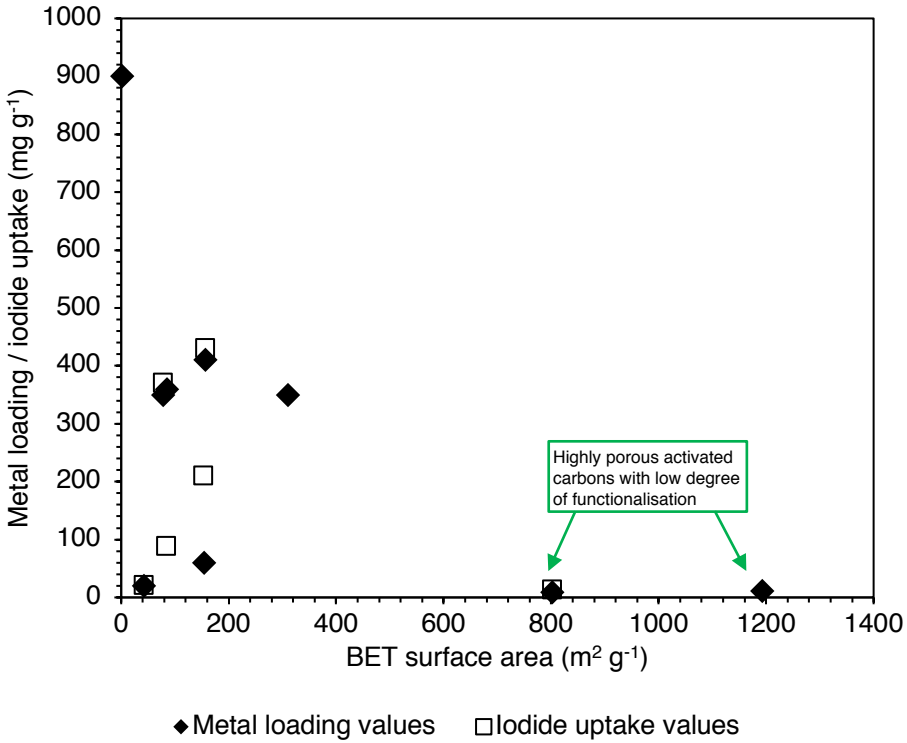


**Figure S1.** Relationships between measured BET surface areas of adsorbents with extent of metal-loading and iodide uptake capacity.

## References

[1] R.M. Asmussen, J.J. Neeway, A.R. Lawter, A. Wilson, N.P. Qafoku, Silver-based getters for I-129 removal from low-activity waste, *Radiochimica Acta*, 104 (2016) 905-913.
[2] T. Karanfil, E.C. Moro, S.M. Serkiz, Development and testing of a silver chloride-impregnated activated carbon for aqueous removal and sequestration of iodide, *Environmental Technology*, 26 (2005) 1255-1262.
[3] X.Y. Zhang, P. Gu, X.Y. Li, G.H. Zhang, Efficient adsorption of radioactive iodide ion from simulated wastewater by nano $Cu_2O$/Cu modified activated carbon, *Chemical Engineering Journal*, 322 (2017) 129-139.

[4] C. Decamp, S. Happel, Utilization of a mixed-bed column for the removal of iodine from radioactive process waste solutions, *Journal of Radioanalytical and Nuclear Chemistry*, 298 (2013) 763-767.
[5] T.J. Robshaw, S.M. Griffiths, A. Canner, J.P. Bezzina, D.B. Hammond, S. Van Meurs, M.D. Ogden, Insights into the interaction of iodide and iodine with Cu(II)-loaded bispicolylamine chelating resin and applications for nuclear waste treatment, *Chemical Engineering Journal*, 390 (2020) 124647-124659.
[6] Z. Tauanov, V.J. Inglezakis, Removal of iodide from water using silver nanoparticles-impregnated synthetic zeolites, *Science of the Total Environment*, 682 (2019) 259-270.
[7] A. Bo, S. Sarina, Z.F. Zheng, D.J. Yang, H.W. Liu, H.Y. Zhu, Removal of radioactive iodine from water using $Ag_2O$ grafted titanate nanolamina as efficient adsorbent, *Journal of Hazardous Materials*, 246 (2013) 199-205.
[8] S.S. Liu, N. Wang, Y.C. Zhang, Y.R. Li, Z. Han, P. Na, Efficient removal of radioactive iodide ions from water by three-dimensional $Ag_2O$-Ag/$TiO_2$ composites under visible light irradiation, *Journal of Hazardous Materials*, 284 (2015) 171-181.
[9] R.M. Asmussen, J. Matyas, N.P. Qafoku, A.A. Kruger, Silver-functionalized silica aerogels and their application in the removal of iodine from aqueous environments, *Journal of Hazardous Materials*, 379 (2019).
[10] Y.Y. Chen, S.H. Yu, Q.Z. Yao, S.Q. Fu, G.T. Zhou, One-step synthesis of $Ag_2O$@$Mg(OH)_2$ nanocomposite as an efficient scavenger for iodine and uranium, *Journal of Colloid and Interface Science*, 510 (2018) 280-291.
[11] P. Mao, Y. Liu, Y. Jiao, S.W. Chen, Y. Yang, Enhanced uptake of iodide on Ag@$Cu_2O$ nanoparticles, *Chemosphere*, 164 (2016) 396-403.
[12] S.W. Liu, S.H. Kang, H.M. Wang, G.Z. Wang, H.J. Zhao, W.P. Cai, Nanosheets-built flowerlike micro/nanostructured $Bi_2O_{2.33}$ and its highly efficient iodine removal performances, *Chemical Engineering Journal*, 289 (2016) 219-230.
[13] G. Lefevre, M. Alnot, J.J. Ehrhardt, J. Bessiere, Uptake of iodide by a mixture of metallic copper and cupric compounds, *Environmental Science & Technology*, 33 (1999) 1732-1737.
[14] P. Mao, L.Y. Qi, X.D. Liu, Y. Liu, Y. Jiao, S.W. Chen, Y. Yang, Synthesis of Cu/$Cu_2O$ hydrides for enhanced removal of iodide from water, *Journal of Hazardous Materials*, 328 (2017) 21-28.
[15] H. Kodama, Removal of iodide ion from simulated radioactive liquid waste, *Czechoslovak Journal of Physics*, 49 (1999) 971-977.