Electronic Supplementary Material (ESI) for Environmental Science: Nano.

REDUCING ENVIRONMENTAL IMPACTS OF METAL (HYDR)OXIDE NANOPARTICLE EMBEDDED ANION EXCHANGE RESINS USING ANTICIPATORY LIFE CYCLE ASSESSMENT

SUPPLEMENTAL INFORMATION

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Nanocomposite Sorbent Pollutant Removal Capacity

Pollutant removal capacity for each nanocomposite formulation was determined via pseudo-equilibrium testing. For each sorbent, at least five 500 mL amber bottles were filled with synthetic groundwater spiked to 2 μM of both Cr(VI) and As(V) (100 μg/L Cr and 140 μg/L As). Synthetic groundwater was prepared as described (NSF 2007) including 20 mg/L SiO_2, 180 mg/L HCO_3^{1-}, 50 mg/L SO_4^{2-}, 2.0 mg/L NO_3^{1-}-N, 1.0 mg/L F^{1-}, 0.04 mg/L PO_4^{3-}-P, and 71 mg/L Cl^{1-}. This challenging water matrix was used so that performance in most real groundwaters would exceed results shown here. Bottles were dosed with 30 to 450 mg/L sorbent (dry weight). The bottles were shaken and allowed to equilibrate for 7 days. Total Cr and total As were analyzed by inductively coupled plasma optical emission spectroscopy (ICPOES, Thermo iCAP6300). Other anions were analyzed by ion chromatography (Dionex ICS 2000). Isotherm data were analyzed by the Fruendlich isotherm model (Equation 1) with best-fit lines through experimental data for the equilibrium oxyanion concentration, C_e, and sorption capacity, q_e.

$$q_e = K * C_e^{1/n} \qquad (1)$$

Inventory Development

The isotherm parameters modeling the pollutant removal capacity results for each of the sorbents tested is shown in SI Table 1. This was then used to calculate the required mass of sorbent to treat the functional unit. Following the original synthesis procedures, the Fe-AX has an estimated removal capacity of 490 μg Cr g^{-1} and 172 μg As g^{-1} at the pollutant concentration of interest. Therefore, treating 20 million gallons of water would require 1,800 kg of sorbent if determined by Cr capacity or 5,300 kg if determined by As capacity. The larger was selected because it would be unacceptable to continue using the resin after As capacity was exhausted even if it was still removing Cr. The improved synthesis method for Fe-AX yielded a sorbent with 300 µg Cr g^{-1} and 510 µg As g^{-1} removal capacity. It was therefore limited by Cr capacity and requires 3,040 kg of sorbent to treat the functional unit worth of water. The original Ti-AX had 630 µg Cr g^{-1} and 600 µg As g^{-1} removal capacity requiring 1,500 kg sorbent. The improved Ti-AX had 510 µg Cr g^{-1} and 500 µg As g^{-1}, requiring 1,800 kg sorbent. The AX had a Cr capacity of 310 µg Cr g^{-1} requiring 2,900 kg of sorbent to treat the functional unit. Another study found the metal oxide (MO) sorbent had an As capacity of 280 µg g^{-1} (Westerhoff et al. 2005) requiring 3,200 kg to treat the functional unit. The MB option includes both the 2,900 kg of AX and the 3,200 kg of MO.

The bulk weight of moist resin is 1.1 kg per liter (Rohm & Haas 2008), which was used to convert the required mass of resin calculated in Section 2.1 to a volume. The contact vessel containing the sorbent was assumed to be cylindrical with a height:diameter aspect ratio of 3:1. It was more reasonable to assume a constant aspect ratio than constant diameter to stay within typical design parameters because a larger resin volume would likely be used in a larger diameter vessel to avoid an overly tall vessel. The original Fe-AX vessel was therefore estimated to be 4.2 feet in diameter and 12 feet tall. The original Ti-AX vessel was 2.7 feet in diameter and 8.2 feet tall. The MB vessel was 4.4 feet in diameter and 13 feet tall.

Pump power demand was estimated with the vessel dimensions according to Equation 2.

$$P=Q\,\rho\,g\,H\,\eta^{-1} \qquad (2)$$

where P was pump power in kW, Q was water flow rate in gallons min^{-1}, ρ was water density in lb ft^{-3}, g was gravitational acceleration in ft s^{-2}, H was headloss through the resin in ft, and η is pump efficiency. The flow rate defined in Section 2.1 was 20 MG per year, equivalent to 38 gallons min^{-1}. Water density was 62.4 lb ft^{-3}, and gravity was 32.2 ft s^{-2}. Headloss in the resin bed at a loading rate of 10 gal min^{-1} ft^{-2} is 2.25 psi per foot of bed depth (Rohm & Haas 2008), equivalent to 5.19 feet of head per foot of bed depth. Pump efficiency was assumed to be 60%. Using the separate bed depths of the three treatment options yielded required pump power for Fe-AX as 0.77 kW, 0.51 kW for Ti-AX, and 0.81 for MB. These were equivalent to 6,800 kW hr for Fe-AX, 4,500 kW hr for Ti-AX, and 7,100 for MB over the course of one year.

Exclusions from System Boundary. The system boundary excluded materials of the treatment plant itself such as piping, valves, and contactor vessels. These materials would be required for physical operation of the water treatment technology but were only loosely attributable to the choice of sorbent itself. Previous studies have indicated environmental impacts from treatment plant construction range between negligible (Raluy et al. 2005) to 4–9% (Stokes and Horvath 2006).

No pH control chemicals were included because the sorption capacities for each sorbent were reported for ambient pH. Each of the treatment options would perform better at depressed pH, but the relative benefit was assumed the same for each option and therefore excluded from this comparison.

Transportation of the resin was excluded across the life cycle, including moving the parent resin to the place of manufacture, transporting the hybrid resin to the water treatment site, and hauling exhausted resin away from the site. This is because impacts would vary widely based on an arbitrary assumption for treatment location, and they would not vary greatly between scenarios. Prior studies found that material delivery for a water treatment facility contributed less than 0.6% of total emissions (Stokes and Horvath 2006) and less than 2% of total global warming equivalents (Stokes and Horvath 2011).

Impacts associated with the water supply are excluded. Items such as well pumping, source water depletion, and distribution pumping are excluded. This LCA focused on differentiating treatment strategies, and impacts from those items would not vary.

Matching Impact Factors

An impact factor for a general anion exchange resin was used (Anion Exchange Resin – Synthesis). It represents a strong base anion exchange resin made of polystyrene, functionalized with chloromethyl methyl ether and trimethylamine, and containing 50% moisture. The three treatment options being studied used a weak base anion exchange resin made of phenol-formaldehyde polycondensate, had undergone an unknown functionalization, and had 60% moisture content (Rohm & Haas 2008). Though not exact matches, it was deemed appropriately representative for an impact factor since they are both organic polymer structures with some form of functionalization and high moisture content.

The chemical inventory items correlated closely with impact factors. Sulfuric acid, ferric chloride, sodium hydroxide, methanol, and sodium chloride each had impact factors with matching CAS numbers and descriptions. The titanium oxysulfate precursor was matched with the impact factor for titanium dioxide via sulfate production process.

Electricity impact factors were a supply mix, medium voltage, at grid, with average United States production data.

Model Sensitivity

SI Figure 2 depicts results of the model sensitivity analysis relative to change in climate change potential from changes in various inputs. The following paragraphs describe changes in model results for all impact categories from changes to various model imputs.

Doubling the sorbent capacity, representing either an improvement in sorbent performance or a decreased competition from co-occurring constituents in the source water, had the effect of lowering final impacts by 33%–50% compared to the base case (ranges reported depending on sorbent and environmental impact category). Cutting the assumed sorbent capacity in half, representing either lower than expected sorbent performance or strong interference from co-occurring constituents in the source water, raised final impacts by 57%–100%.

If the functional unit doubled to 40 MG, final impacts rose by 100%–130% of the base case. If the functional unit was cut in half to 10 MG, final impacts were lowered by 50%–56%.

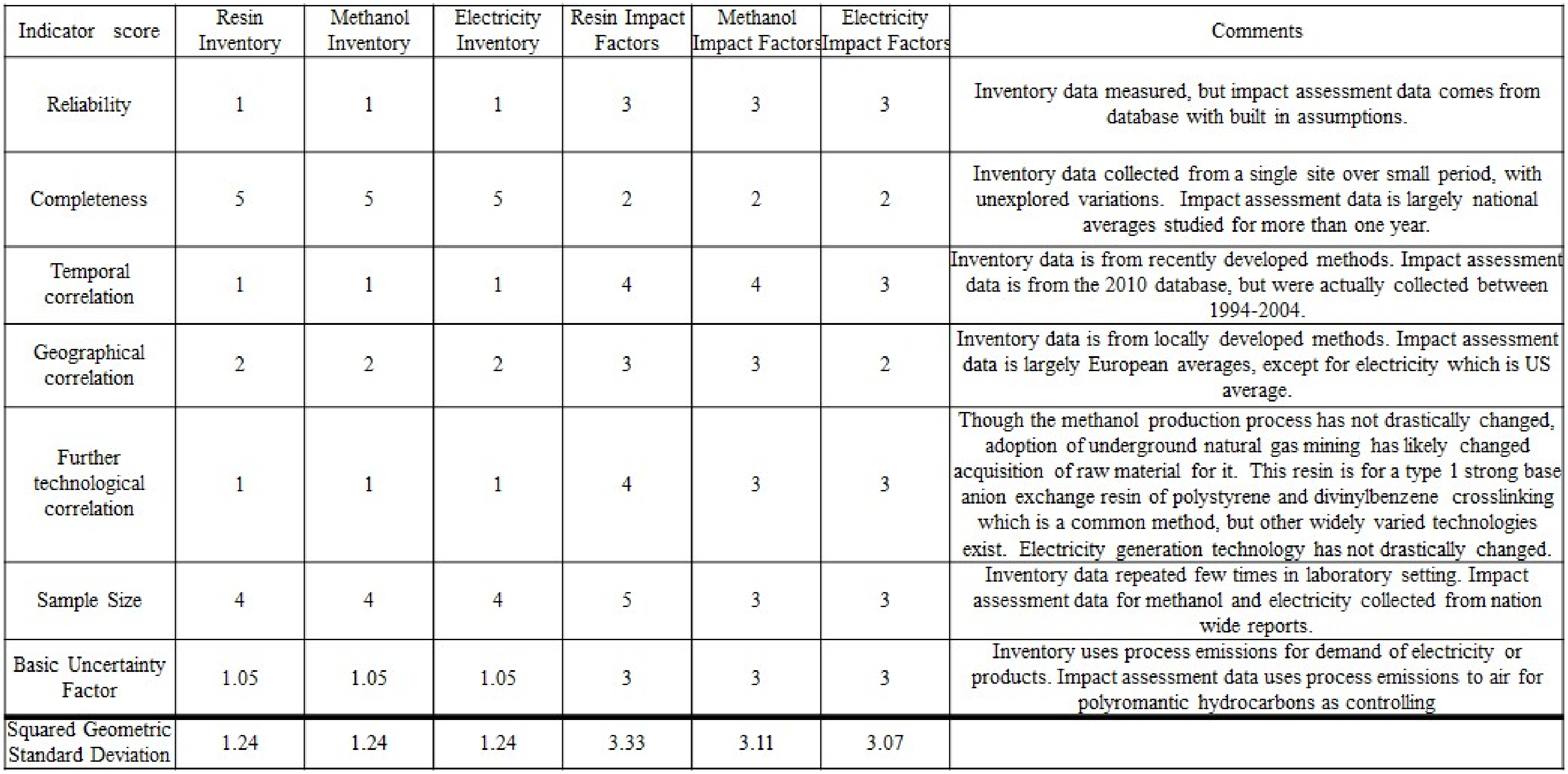
If the influent pollutant concentration were lowered to 15 μg L^{-1} instead of 20 μg L^{-1}, the final impacts lowered by 27%–42%. If the influent pollutant concentration were raised to 30 μg L^{-1}, the final impacts raised by 48%–83%.

If synthesis methods for Fe-AX could be improved such that only half as much methanol was required, the associated life cycle impacts reduced by 0%–12% of the base case. If the synthesis methods for Ti-AX could be improved to only require half as much oven heating time for nanoparticle hydrolysis, the associated life cycle impacts reduced by 0%–23% of the base case. If methods for the synthesis of the parent AX resin could be improved such that the environmental impact of their synthesis were cut in half, the life cycle impacts of Ti-AX and Fe-AX lowered by 6%–50% of the base case. If electricity generation methods were be improved to cut the impacts in half, the life cycle impacts of the nanocomposite sorbents reduced by 0%–42%.

If Brazilian electricity generation was considered, the change in life cycle impacts of the nanocomposite sorbents ranged from reducing by 79% to increasing by 8% compared to using US electricity, with a median change of 23% reduction. If German electricity generation is used the impacts reduced by 0%–63%, with a median 15% reduction. If a Chinese electricity generation mix is used, the impacts changed ranging from a 66% decrease to a 102% increase compared to using US electricity generation with a median 9% increase. Ecotoxicity and non-cancer human toxicity were reduced for all sorbents by using Chinese electricity compared to US, and the largest comparative increases in impacts were in human respiratory effects and ocean acidification.

Sorbent	Fruendlich Isotherm Parameters						Removal Capacity			Sorbent Required (kg)
	Cr			As						
	K	1/n	R^2	K	1/n	R^2	Ce (µM)	Q_{Cr} (µmol/g)	Q_{As} (µmol/g)	
Original Fe-AX	1.50	1.70	0.93	9.40	1.13	0.77	0.2	9.5	2.3	5,272
Improved Fe-AX	9.68	0.33	0.79	11.90	0.35	0.98	0.2	5.7	6.8	3,044
Ti-AX 24Hr	21.23	0.35	0.70	10.82	0.18	0.42	0.2	12.2	8.0	1,508
Ti-AX 16Hr	10.59	0.64	0.89	6.08	0.27	0.93	0.2	3.8	3.9	4,614
Ti-AX 8Hr	19.70	0.43	0.70	13.96	0.49	0.64	0.2	9.8	6.3	1,925
Ti-AX 4Hr	16.92	0.34	0.98	13.09	0.42	0.97	0.2	9.8	6.7	1,810
AX	17.27	0.66	0.80	n/a	n/a	n/a	0.2	6.0	n/a	2,917
*MO									3.7	3,242

SI Table 1: Sorbent data used to calculate mass required to treat the functional unit. K is in units of (µmol/g)(µM)$^{-1/n}$. *MO capacity was taken from (Westerhoff et al. 2005) and represents granular ferric hydroxide sorbent in simulated groundwater.

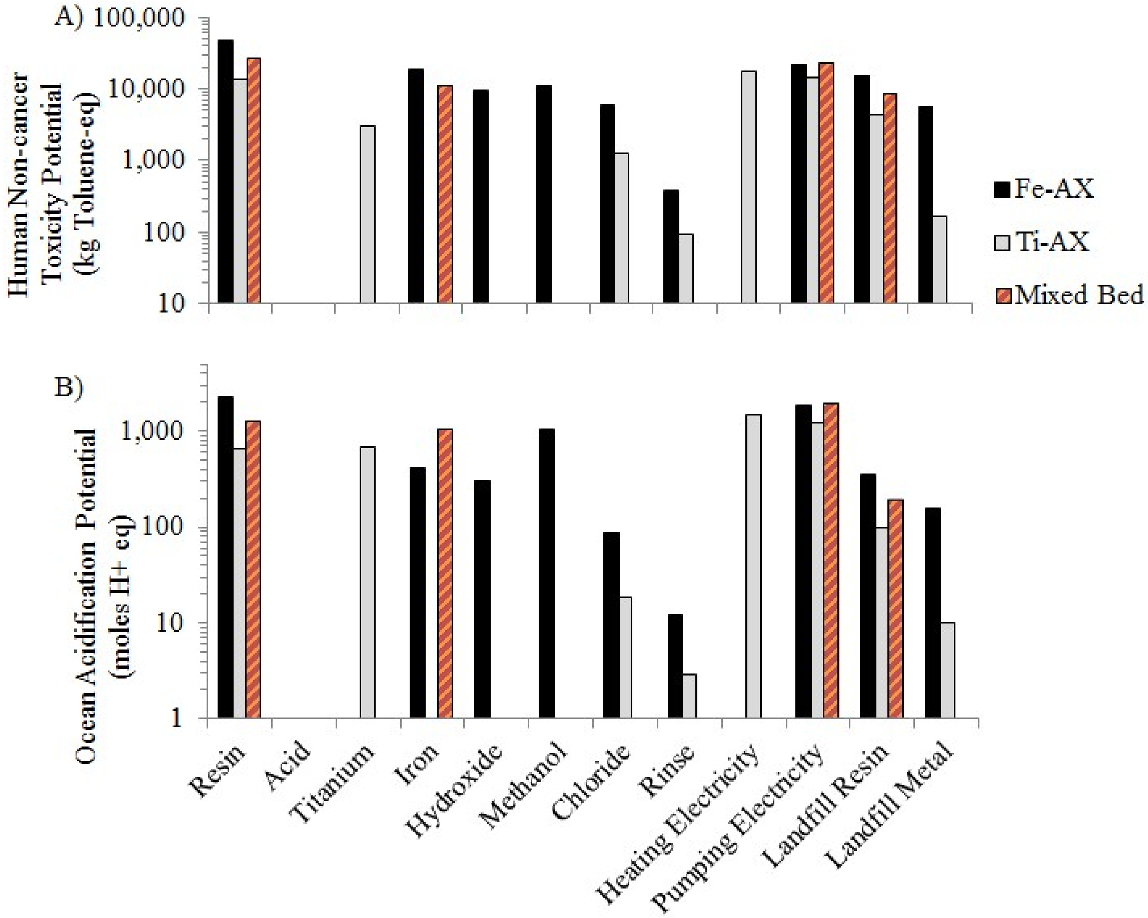


Indicator score	Resin Inventory	Methanol Inventory	Electricity Inventory	Resin Impact Factors	Methanol Impact Factors	Electricity Impact Factors	Comments
Reliability	1	1	1	3	3	3	Inventory data measured, but impact assessment data comes from database with built in assumptions.
Completeness	5	5	5	2	2	2	Inventory data collected from a single site over small period, with unexplored variations. Impact assessment data is largely national averages studied for more than one year.
Temporal correlation	1	1	1	4	4	3	Inventory data is from recently developed methods. Impact assessment data is from the 2010 database, but were actually collected between 1994-2004.
Geographical correlation	2	2	2	3	3	2	Inventory data is from locally developed methods. Impact assessment data is largely European averages, except for electricity which is US average.
Further technological correlation	1	1	1	4	3	3	Though the methanol production process has not drastically changed, adoption of underground natural gas mining has likely changed acquisition of raw material for it. This resin is for a type 1 strong base anion exchange resin of polystyrene and divinylbenzene crosslinking which is a common method, but other widely varied technologies exist. Electricity generation technology has not drastically changed.
Sample Size	4	4	4	5	3	3	Inventory data repeated few times in laboratory setting. Impact assessment data for methanol and electricity collected from nation wide reports.
Basic Uncertainty Factor	1.05	1.05	1.05	3	3	3	Inventory uses process emissions for demand of electricity or products. Impact assessment data uses process emissions to air for polyromantic hydrocarbons as controlling
Squared Geometric Standard Deviation	1.24	1.24	1.24	3.33	3.11	3.07	

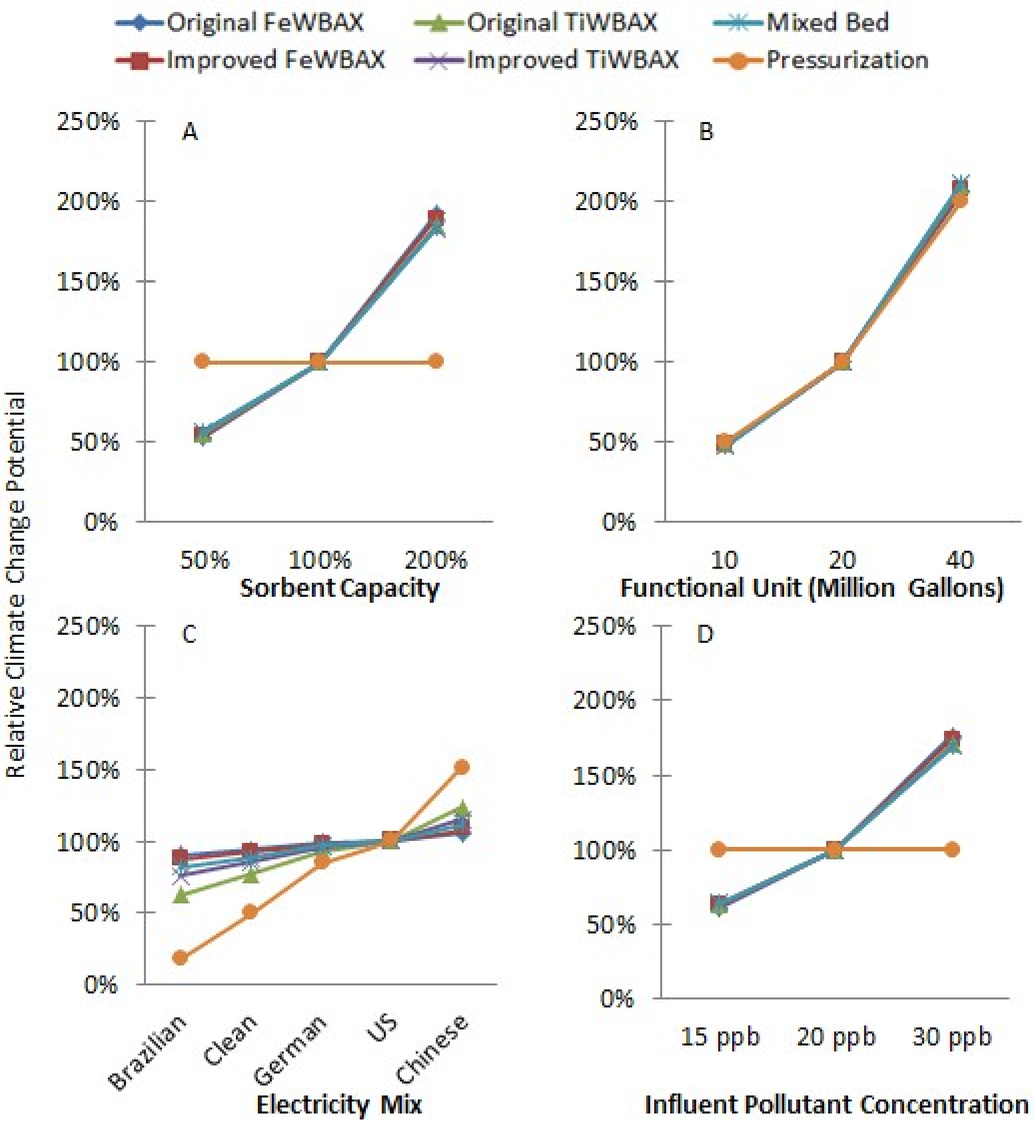
SI Table 2. Data Quality Assessment. The inventory and impact assessment factor quality for the three highest contributing items were analyzed. A score of 1 represents the data used has high reliability, and a score of 5 represents low reliability. These are converted to uncertainty factors and combined to produce a squared geometric standard deviation.

	Acidification (moles H+ Eq)	Ecotoxicity (kg 2,4-D Eq)	Eutro-phication (kg N)	Global Warming (kg CO2 Eq)	Ozone Depletion (kg CFC-11 Eq)	Photo-chemical Oxidation (kg NOx Eq)	Carcin-ogenics (kg Benzene Eq)	Non-Carcinogenics (kg Toluene Eq)	Respiratory Effects (kg PM2.5 Eq)
Original Fe-AX Synthesis	7.89E-01	1.03E+00	2.15E-03	6.54E+00	1.73E-04	8.92E-03	1.26E-02	1.79E+01	3.10E-03
Original Fe-AX Disposal	9.58E-02	1.07E-01	1.82E-04	1.50E+00	1.09E-08	1.75E-03	2.76E-03	3.94E+00	2.61E-04
Improved Fe-AX Synthesis	9.38E-01	1.04E+00	2.16E-03	6.57E+00	1.73E-04	9.10E-03	1.28E-02	1.82E+01	3.79E-03
Improved Fe-AX Disposal	9.58E-02	1.07E-01	1.82E-04	1.50E+00	1.09E-08	1.75E-03	2.76E-03	3.94E+00	2.61E-04
Original Ti-AX Synthesis	1.88E+00	2.56E+00	2.08E-03	7.55E+00	1.72E-04	1.28E-02	1.42E-02	2.39E+01	7.55E-03
Original Ti-AX Disposal	7.25E-02	2.69E-02	1.63E-04	1.34E+00	7.69E-09	1.45E-03	2.72E-03	2.99E+00	1.42E-04
Improved Ti-AX Synthesis	1.06E+00	9.76E-01	1.79E-03	5.24E+00	1.72E-04	8.40E-03	1.06E-02	1.41E+01	4.27E-03
Improved Ti-AX Disposal	7.25E-02	2.69E-02	1.63E-04	1.34E+00	7.69E-09	1.45E-03	2.72E-03	2.99E+00	1.42E-04

SI Table 3. Proposed impact factors for 1 kg of Fe-AX and Ti-AX according to synthesis phase and disposal phase.



SI Figure 1. Hotspot analysis of original Fe-AX, original Ti-AX, and mixed bed showing impact contributions of individual inventory items to A) human non-carcinogenic toxicity potential and B) ocean acidification potential.



SI Figure 2. Sensitivity analysis depicting how a change in model inputs changes the resultant climate change potential. Includes if A) the sorbent capacity is halved or doubled, B) the functional unit is halved or doubled, C) if a different electricity mix is chosen (including a theoretical "Clean" energy mix with impacts for electricity halved compared to the base case), and D) if the influent pollutant concentration is halved or doubled.

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