

Selective Removal of Nitrosamines from a Model Amine Carbon Capture Waterwash using Low Cost Activated Carbon Sorbents

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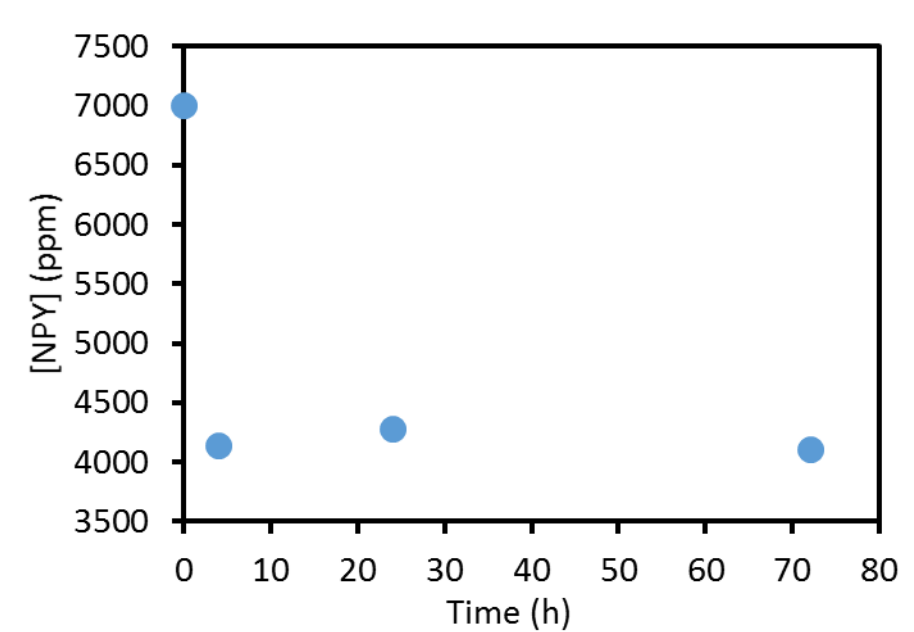


Figure S1. Effect of extended circulation time on NPY absorption. No additional absorption is observed, indicating system is at equilibrium within 4h.

Effect of solution content and sorbent on pH of model waterwash solutions. The pH of aqueous solutions is well known to effect the absorption behavior of organic compounds by carbon sorbents. The pH of representative model waterwash solutions was therefore measured, verifying that no significant change is present between the model waterwash samples examined in this study. The pH of 0.3 wt.% MEA and 1 wt.% Pz is very close (11.34 and 11.53, respectively). When 1000 ppm NPY is added to 0.3 wt.% MEA, the pH is unchanged at 11.32. Carbon sorbents tested in simulated washwater conditions for this study were pre-wetted before exposure to the analyte-containing solution, which may also serve to pre-equilibrate the surface to the process-relevant conditions. When 500 mL of 0.3 wt.% MEA (pH = 11.34) is circulated through pre-wetted carbon beds (5 g) for 4 h, the pH of the resulting solution is again not altered significantly. Commercial coconut charcoal decreases the pH of the solution to a pH of 11.30, while the acid treated coconut charcoal (with the most dramatic pH difference) only decreases the solution to 11.06. We therefore conclude that over the course of the simulated washwater experiments, the pH is not sufficiently altered by added nitrosamine or the sorbent to affect absorption behavior.

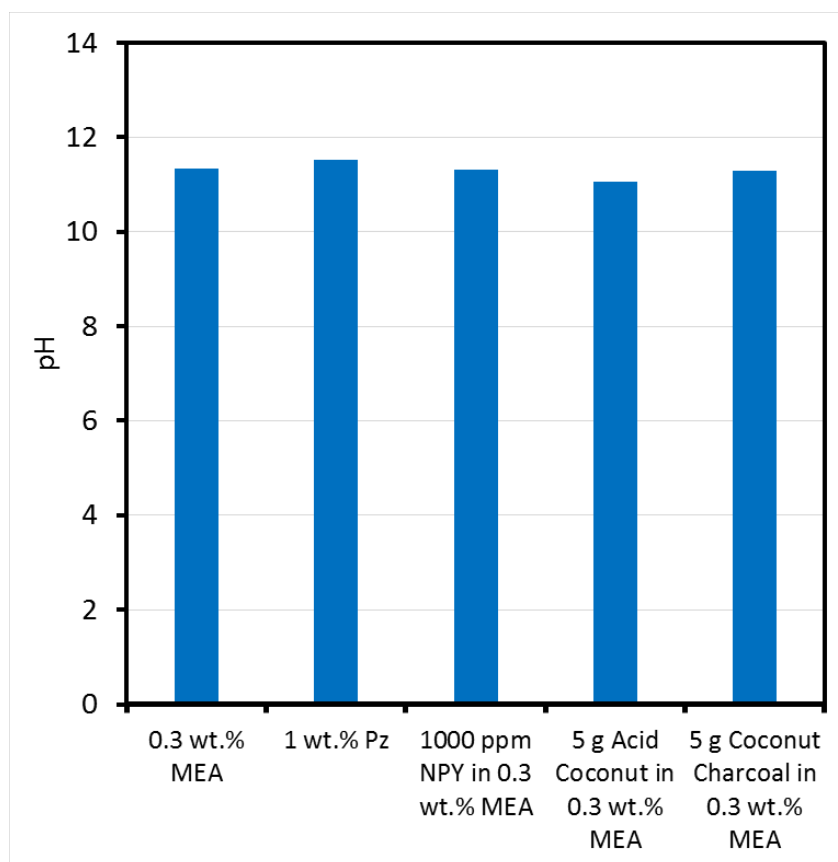


Figure S2. pH of representative model washwater solutions

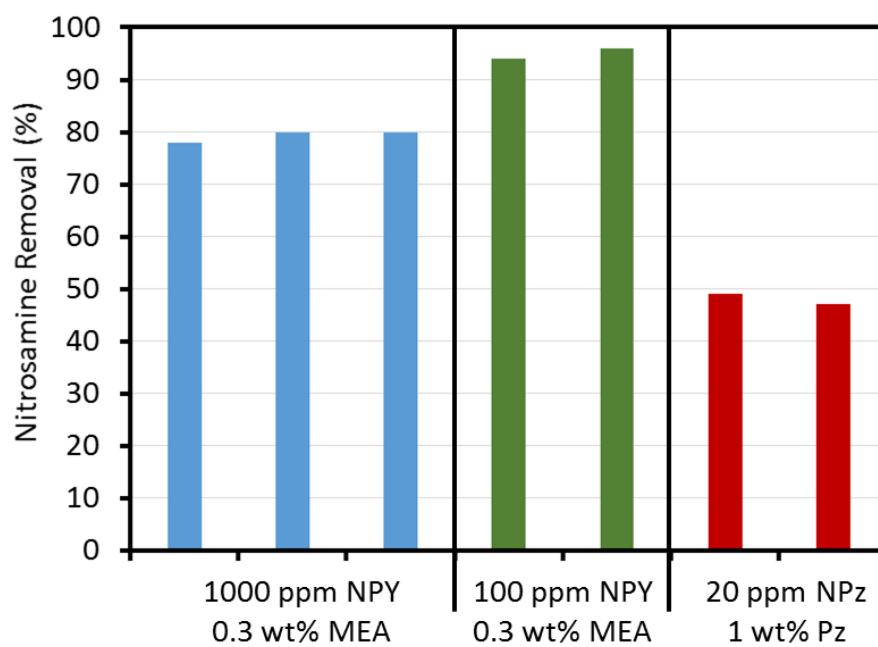


Figure S3. Representative replicate experiments for nitrosamine absorption by commercial coconut charcoal.

Table S1. Surface Composition of Carbon Sorbents by EDS

Element	Commercial Coconut Charcoal	Thermal Coconut Charcoal	Acid Coconut Charcoal	Commercial Activated Carbon	Thermal Activated Carbon
C	92.11	80.56	76.13	88.48	87.31
O	5.25	14.11	23.87	6.75	8.16
Na	0.25	0.27	-	-	-
Mg	0.26	0.24	-	-	-
Al	-	-	-	1.12	1.13
Si	0.58	0.33	-	2.21	2.08
P	0.25	-	-	-	-
K	1.31	-	-	-	-
S	-	0.34	-	0.87	0.87
Fe	-	-	-	0.56	0.45
Cl	-	0.20	-	-	-
K	-	2.85	-	-	-
Ca	-	0.40	-	-	-

Table S2. Calculated parameters and error from Langmuir and Freundlich isotherms.

carbon type	Langmuir					Freundlich				
	q_m	Std. Error*	k_L	Std. Error*	R^2	n	Std. Error*	k_F	Std. Error*	R^2
commercial coconut charcoal	191.43	8.98	0.0035	0.0007	0.991	3.41	0.53	17.27	6.00	0.975
oxidized coconut charcoal	132.75	1.30	0.0094	0.0006	1.000	3.80	1.62	17.57	1.22	0.905
acid coconut charcoal	17.49	17.49	0.0011	0.0036	0.570	2.46	3.23	0.52	2.15	0.524
commercial activated carbon	113.19	5.03	0.0094	0.0029	0.995	3.79	1.78	15.47	13.53	0.877
oxidized activated carbon	128.64	6.78	0.0069	0.0021	0.993	3.77	1.53	16.71	1.30	0.914

* Weighted standard error from SigmaPlot (version 13.0)

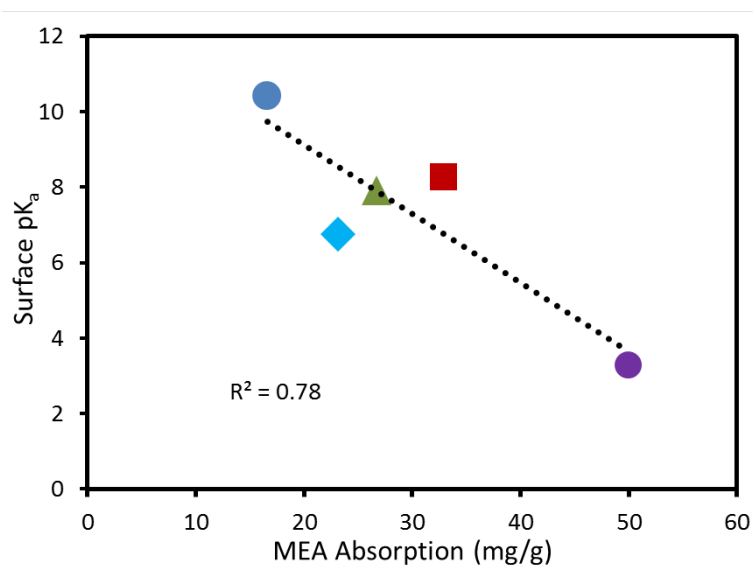


Figure S4. Relationship between surface pK_a and MEA adsorption of carbon sorbents without added nitrosamine.

Nitrosation catalyzed by activated carbon surface: Control experiments were conducted to ensure the surface of the activated carbon sorbents do not catalyze nitrosamine formation. The carbon sorbents were soaked in relevant piperazine washwater (1 wt.% Pz) for 72 h and the liquid phase was analyzed for nitrosopiperazine (NPZ). These data are shown in Figure S5, shown relative to the commercial coconut charcoal sample with a 0.1 ppm NPZ spike (dark blue). There is no significant NPZ formation observed that would cause any variation in the experimental data. The secondary amine PZ was selected for these control experiments because it can directly form a nitrosamine, unlike the primary amine solvent MEA.

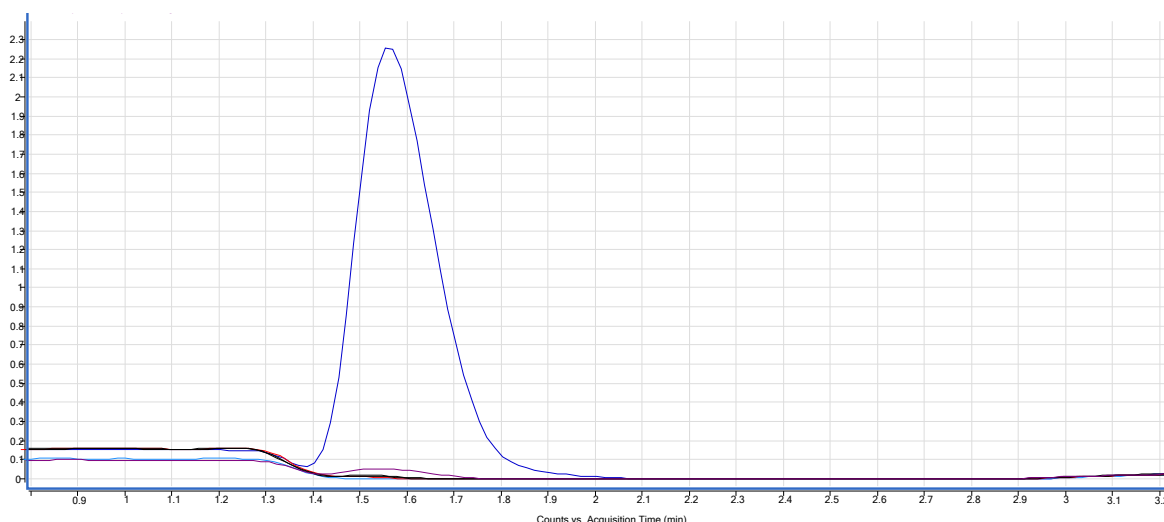


Figure S5. LC-MS of 1 wt.% Pz exposed to activated carbon sorbents for 72 h. (dark blue = commercial coconut charcoal + 0.1 ppm NPZ spike, green = commercial coconut charcoal, red = oxidized coconut charcoal, purple = acid coconut charcoal, light blue = commercial activated carbon, black = oxidized activated carbon). Y-axis response is $\times 10^5$.