**Synergy Effect of Nitrogen and Molybdenum on Activated Carbon Matrix for Selective Adsorptive Desulfurization: Insights into Surface Chemistry Modification**

Musa O. Azeez, Abdulkadir Tanimu, Khalid Alhooshani, Saheed A. Ganiyu**\*.**

Department of Chemistry, King Fahd University of Petroleum & Minerals, 31261, Dhahran, Saudi Arabia.

**Supplementary Information**

**EDX analysis of adsorbents**



**Fig. SI-1: EDS images of (a) AC (b) AC-N (c) AC-N-Mo and (d) AC-Mo**

**Table SI-1: Surface atomic percent of elements present in modified carbon.**

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **States** | **C1s** | **C1s** | **N1s** | **N1s** | **N1s** | **O1s** | **O1s** | **O1s** | **O1s** | **Mod3** | **Mod3** | **Mod3** |
| **BE (eV)** | **284.5** | **283** | **396** | **398** | **401.6** | **530.2** | **530.8** | **530.9** | **531** | **227.8** | **230.8** | **233** |
| **AC-N** | 23.7 | 33.66 | 3.33 | - | - | - | 39.31 | - | - | - | - | - |
| **AC-N-Mo** | 16.89 | 32.83 | 1.97 | 0.93 | 0.28 | - | - | 46.8 | - | 0.18 | 0.09 | 0.03 |

**NH3-TPD analysis of sorbents**

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**Fig. SI-2: Surface acidity by ammonia-temperature-programmed desorption (NH3-TPD) of adsorbents (A) AC (B) AC-N (C) AC-N-Mo and (D) AC-Mo**

**Table SI-2: NH3-TPD of the adsorbents**

|  |  |  |
| --- | --- | --- |
| **Adsorbents** | **Temp. (s) (oC)** | **Quantity (mmol/g at STP)** |
| AC | 410, 844 | 4.67, 0.31 |
| AC-N | 485 | 8.03 |
| AC-N-Mo | 421, 856, 935 | 6.23, 1.84 |
| AC-Mo | 214, 400, 847 | 0.22, 2.59, 0.60 |

**Adsorption kinetics**

The Pseudo-first order equation as given by Lagergren 1988 is as shown in equation 3 below.

Where (mg/g) and (mg/g) denote the quantity of sulfur adsorbed at equilibrium and time t (min) respectively, (min-1)represents rate constant for pseudo- first order kinetics.



**Fig. SI-3: Pseudo first order kinetics at the concentration of (a) 50 mg-S/L, (a) 100 mg-S/L, (a) 150 mg-S/L, (a) 200 mg-S/L**

Pseudo-second order equation and the interpretation of the terms are expressed in equation 4 below:

Where (mg/g) and (mg/g) denote the quantity of sulfur adsorbed at equilibrium and time t (min) respectively, (g/(mg-S.min))represents rate constant for pseudo second order kinetics model. The value of and are both obtained from the slope and intercept of the plot of versus t.



**Fig. SI-4: Pseudo second order kinetics at the concentration of (a) 50 mg-S/L, (a) 100 mg-S/L, (a) 150 mg-S/L, (a) 200 mg-S/L**

Intraparticle-diffusion equation as given by Weber and Morris and the interpretation of the terms are given in equation 5 below:

Where (mg/g), (min1/2), (mg/g.min), and represent the quantity of sulfur adsorbed at equilibrium, the square root of the contact time, the intraparticle diffusion rate constant, and boundary layer thickness respectively.



**Fig. SI-5: Intraparticle diffusion at the concentration of 100 mg-S/L**

**Table SI-3: Kinetic parameter of 100 mg-S/L on the investigated adsorbent materials**

|  |  |  |  |
| --- | --- | --- | --- |
| **100 mg-S/L** | **Pseudo-first order** | **Pseudo-second order** | **Intraparticle diffusion** |
| **Adsorbent** | **qe(exp)a** | **qe(cal)a** | **k1(103)b** | **R2** | **qe(cal)a** | **k2(103)c** | **R2** |  | **C** | **R2** |
| **AC** | 17.96 | 2.57 | 2.7 | 0.7573 | 16.92 | 20.6 | 0.9999 | 0.1221 | 14.768 | 0.8270 |
| **AC-N** | 17.84 | 5.89 | 4.6 | 0.9213 | 17.01 | 4.9 | 0.9996 | 0.3579 | 10.404 | 0.9061 |
| **AC-N-Mo** | 19.94 | 6.92 | 2.4 | 0.9221 | 17.15 | 5.7 | 0.9989 | 0.2829 | 11.786 | 0.9340 |
| **AC-Mo** | 17.98 | 3.27 | 4.3 | 0.9760 | 17.42 | 9.5 | 0.9994 | 0.1659 | 14.151 | 0.9581 |

a: (mgS/g), b: (min-1), c: g/(mg-S.min)

**Adsorption Isotherms**

The Langmuir linear equation expressed in equation 6 governs the quantity of DBT adsorbed.

Where (mg/L), (mg/g), (mg/g) and represent equilibrium concentration, sorption capacity, and maximum adsorption capacity, Langmuir constant related to adsorption energy respectively. The expression and are obtained from the slope and intercept of the plot of versus.

The Freundlich isotherm is represented in equation 7 below;

Where KF (mg g-1) and n represents Freundlich constant related to adsorption capacity, and intensity respectively.



**Fig. SI-6: Adsorption isotherm of adsorbents by Langmuir and Freundlich. (Initial conc. = 50-250 mg-S/L contact time = 24 h, adsorbent dosage = 100 mg, and 20 mL solution of isooctane containing DBT)**

**Table SI-4: Isotherm parameters for adsorption of 50-200 ppmw-S DBT on adsorbent materials**

|  |  |
| --- | --- |
| **Langmuir** | **Freundlich** |
| **Adsorbent** | **aqmax** | **bKL** | **R2** |  | **CKF**  | **1/n** | **n** | **R2** |
| **AC** | 41.7 | 0.056 | 0.9713 |  | 4.20 | 0.5246 | 1.88 | 0.9131 |
| **AC-N** | 44.2 | 0.051 | 0.9486 |  | 3.90 | 0.5546 | 1.79 | 0.9384 |
| **AC-N-Mo** | 48.8 | 0.054 | 0.9580 |  | 4.57 | 0.6383 | 1.81 | 0.8878 |
| **AC-Mo** | 46.1 | 0.047 | 0.9223 |  | 3.22 | 0.5397 | 1.61 | 0.9044 |

a: (mgS/g), b: (L/mg), c: (𝑚𝑔(1− 1 /𝑛 ) 𝑆 × 𝐿 1⁄𝑛 × 𝑔 −1)