Adsorptive denitrogenation of fuel over molecularly imprinted poly-2-(1*H*-imidazol-2-yl)-4-phenol microspheres

*M. S. Abdul-quadir[a], R. van der Westhuizen[b], W. Welthagen[b], E. E. Ferg[a], Z. R. Tshentu[a,] and A. S. Ogunlaja[a,]**

[a]*Department of Chemistry, Nelson Mandela University, P.O. Box 77000, Port Elizabeth 6031, South Africa*

[b]*Analytical Technology, Sasol Technology (Pty) Limited, PO Box 1, Sasolburg 1947, South Africa*

Synthesis

Non-imprinted microspheres: 1.86 g of 2-(1*H*-imidazol-2-yl)-4-vinylphenol was dissolved into a solution containing 2 mL of ethylene glycol dimethacrylate and 1 mL of toluene. After homogeneity was achieved, 0.02 g of benzoyl peroxide, was added to the organic mixture. The resulting organic solution was transferred in drops into a 100 mL solution containing polyvinyl alcohol (PVA) (0.025 g) and NaCl (0.07 g) at 80°C and under stirring at 400 rpm. The reaction was allowed to proceed for 7 h under an argon atmosphere, after which the resulting microspheres were collected by filtration process followed by washing with warm methanol. *Anal. Found* (%) FT-IR (cm^{-1}) 3371 υ(O-H), 1726 υ(C=O), 1630 υ(>NH), 1289 υ(C-N), 1148 υ(C-O-C).

Adsorption Protocol for hydrotreated fuel

Adsorption studies for the removal of organonitrogen compounds was carried out by weighing 150 mg of imprinted microspheres (comprising of 50 mg quinoline-imprinted, 50 mg carbazole-imprinted and 50 mg pyrimidine-imprinted microspheres) as adsorbent. Adsorption proceeded under SPE manifold by conditioning imprinted microspheres at a vacuum pressure of 20 inHg with a solution of hexane followed by loading the hydrotreated diesel (3 mL hydrotreated diesel). Cyclohexane was employed to wash interfering molecules from the sorbent and finally N-compounds were eluted by using a mixture of acetonitrile: methanol (1:1).

S1.1 Adsorption Kinetics and Isotherms

Kinetics: The kinetic mechanism that controls the adsorption process under batch study was monitored by using pseudo-first-order model (Eq. 4) and pseudo-second-order model (Eq. 5). In pseudo-first-order model the occupation rate of the adsorption sites is proportional to the number of unoccupied sites, while the pseudo-second-order assumes that adsorption takes place *via* a chemical reaction process i.e. chemisorption process.

$$\log (q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \qquad (4)$$

$$\frac{t}{q_t} = \frac{1}{q_e^2 K_2} + \frac{1}{q_e} t \qquad (5)$$

where q_e and q_t (mg/g) are the amounts of N-compounds adsorbed on the adsorbent at equilibrium and time t, respectively.

Isotherm: The adsorption behaviour of nitrogen compounds on imprinted microspheres was followed using the Langmuir and Freundlich isothermal equations (Eqns. 6 and 7).

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{K_d}{Q_m} \qquad (6)$$

$$log q_e = \frac{1}{n} log C_e + log K \qquad (7)$$

where q_e (mg/g) and C_e (mg/g) are the amount adsorbed at equilibrium and the equilibrium concentration, (Q_m), is the theoretical maximum adsorption capacity at monolayer (mg/g), and K_d is the Langmuir constant (related to the affinity of adsorption sites). Freundlich constants k and n indicating adsorption capacity and intensity respectively were determined from the linear plot of log q_e against log C_e.

DATA

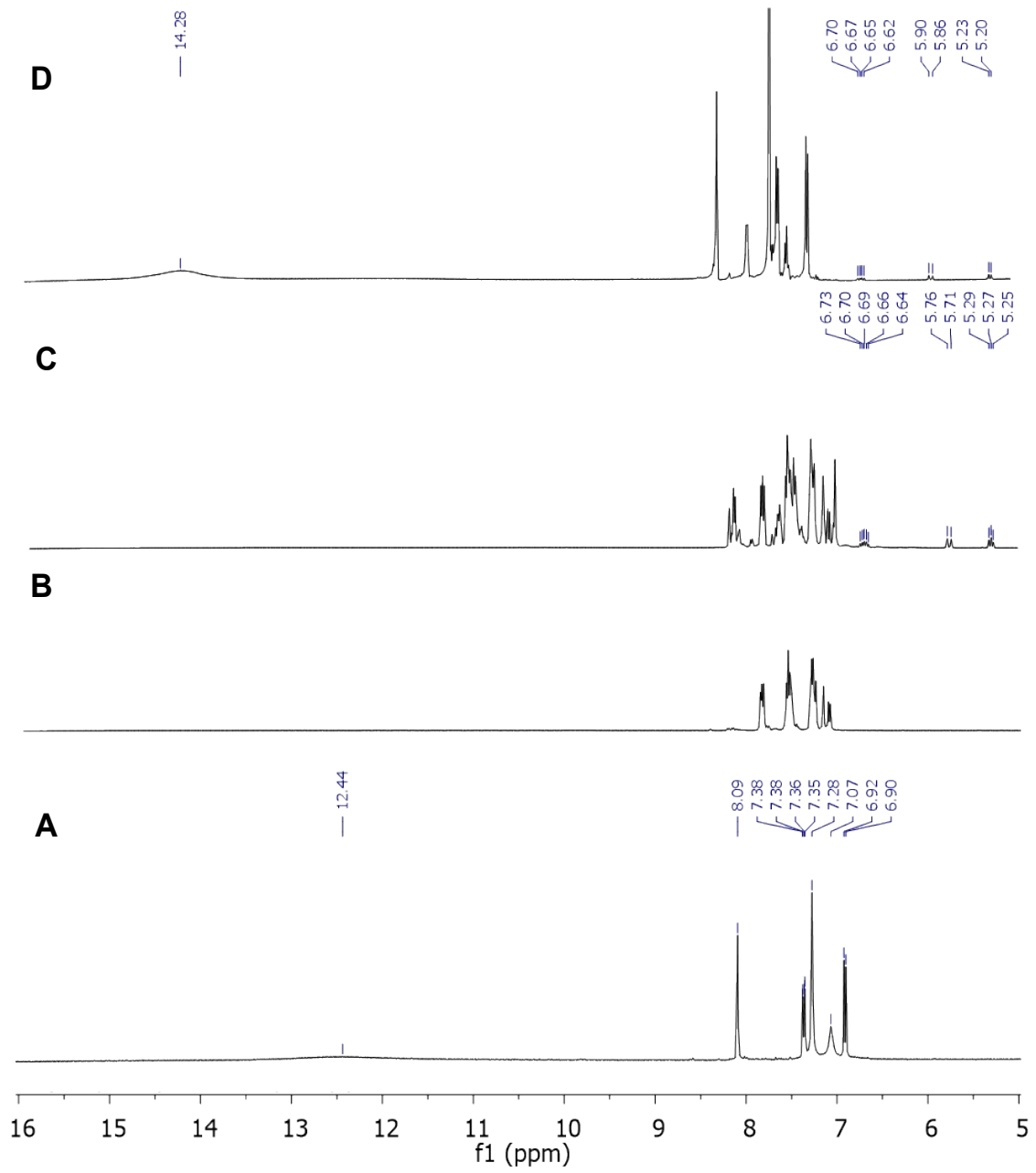


Fig. S1 [1]H-NMR spectra of (A) 4-bromo-2-(1*H*-imidazol-2-yl) phenol, (B) 2-(1-benzoyl-1*H*-imidazol-2-yl)-4-bromophenyl benzoate, (C) 2-(1-benzoyl-1*H*-imidazol-2-yl)-4-vinylphenyl benzoate and (D) 2-(1*H*-imidazol-2-yl)-4-vinyl phenol.

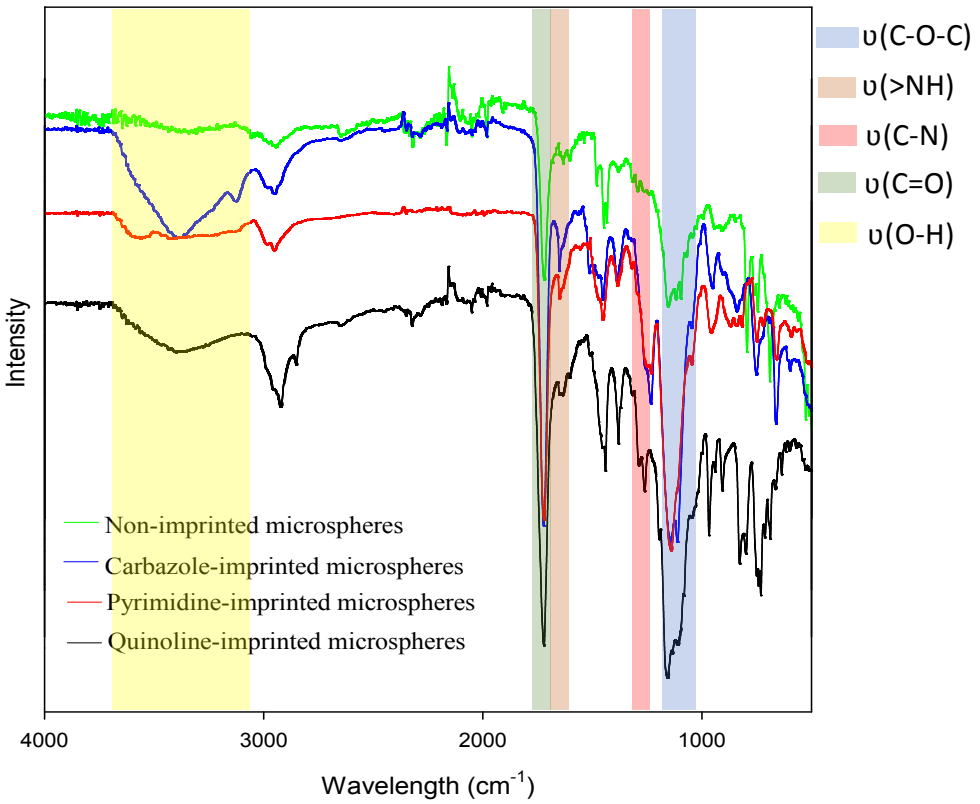


Fig. S2: FTIR spectra of (i) Non-imprinted microspheres (ii) Carbazole-imprinted microspheres (iii) Pyrimidine-imprinted microspheres and (iv) Quinoline imprinted microspheres.

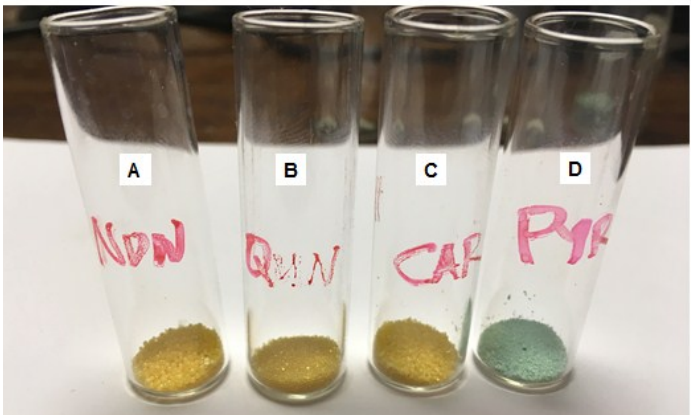


Fig. S3. Images of (A) non-imprinted microspheres, (B) quinoline-imprinted microspheres (QUNMIP), (C) carbazole-imprinted microspheres (CARMIP), and (D) pyrimidine-imprinted microspheres (PYMMIP).

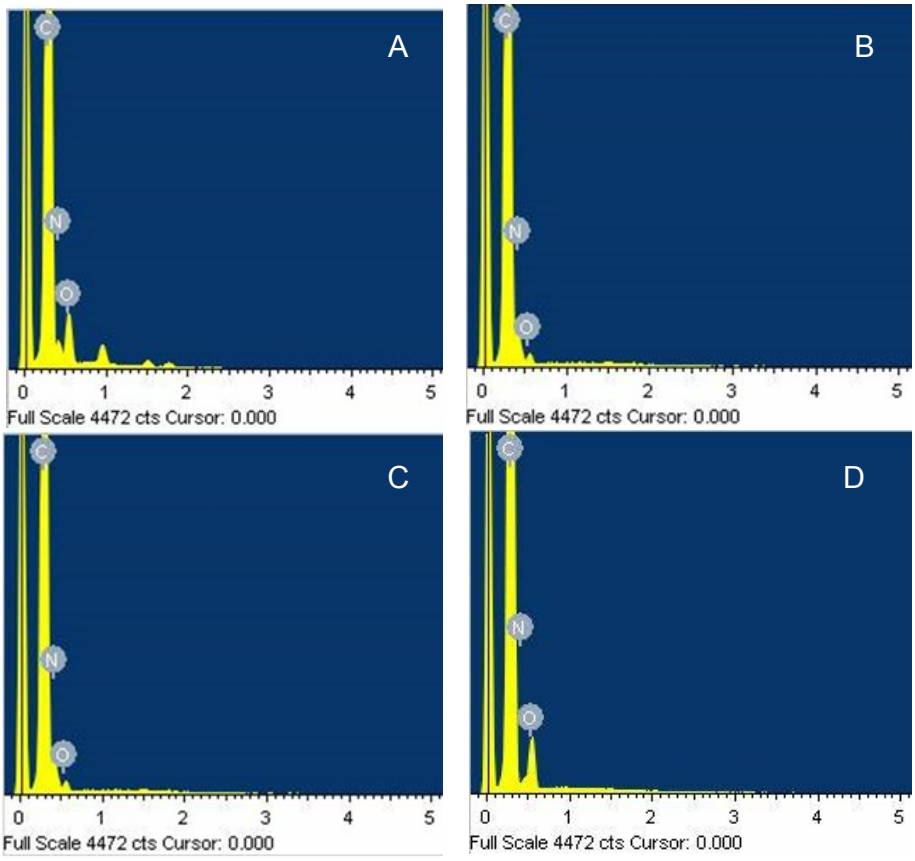


Fig. S4 Energy Dispersive Spectroscopy (EDS) of (a) non-imprinted microspheres, (b) pyrimidine imprinted microspheres, (c) carbazole imprinted microspheres, and (d) quinoline imprinted microspheres.

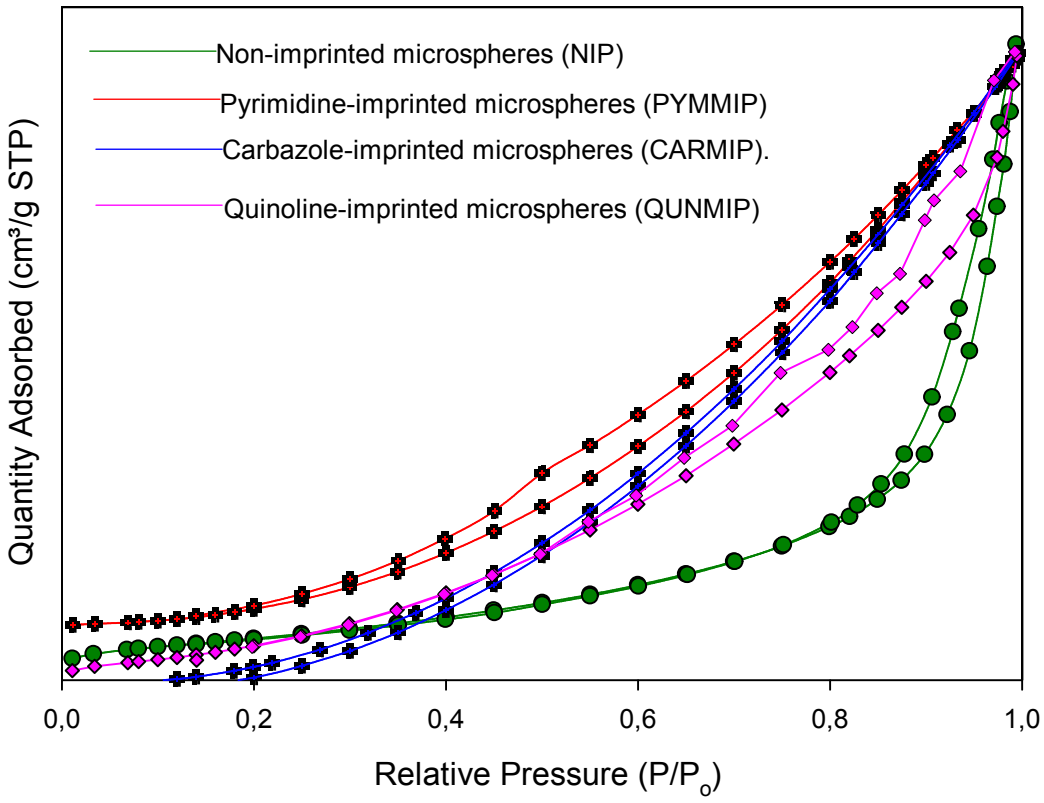


Fig S5. BET Isotherm of (A) Non-imprinted microspheres (NIP), (B) quinoline-imprinted microspheres (QUNMIP), (C) pyrimidine-imprinted microspheres (PYMMIP) and (D) carbazole-imprinted microspheres (CARMIP).

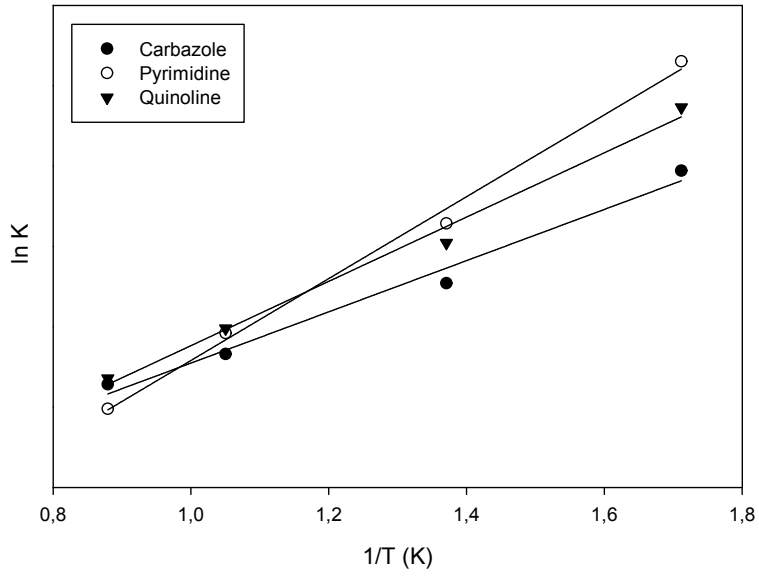


Fig S6. Van't Hoff Plot of adsorption equilibrium constant K_{ad} for adsorption of organonitrogen compounds onto imprinted microspheres.

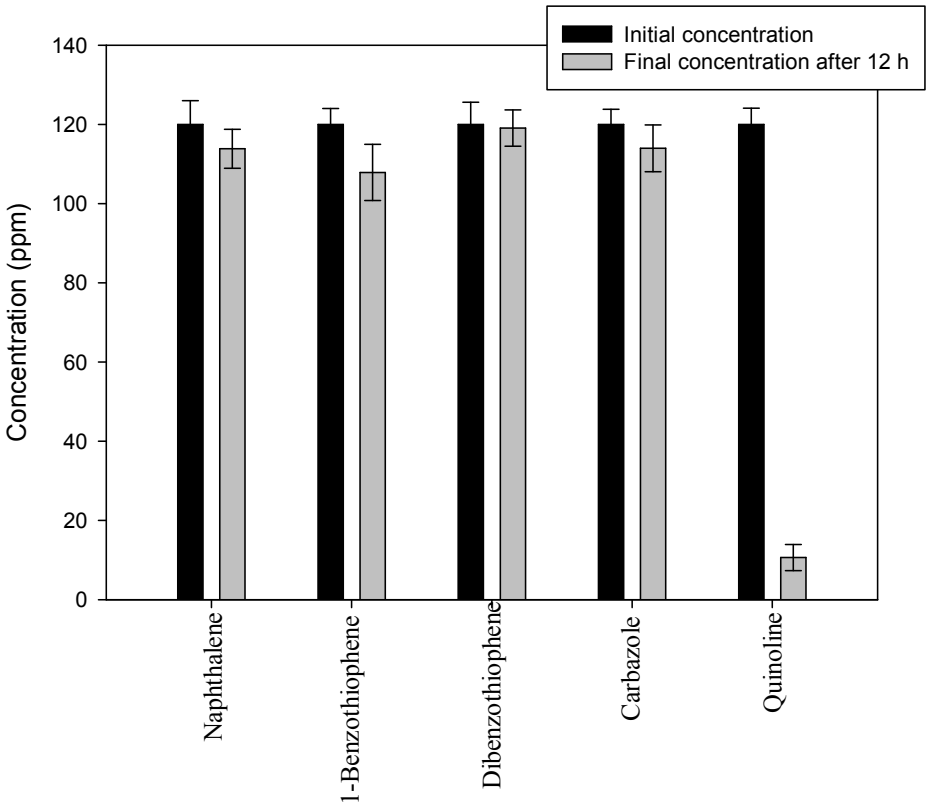


Fig S7. Adsorption selectivity of quinoline using quinoline-imprinted microspheres.

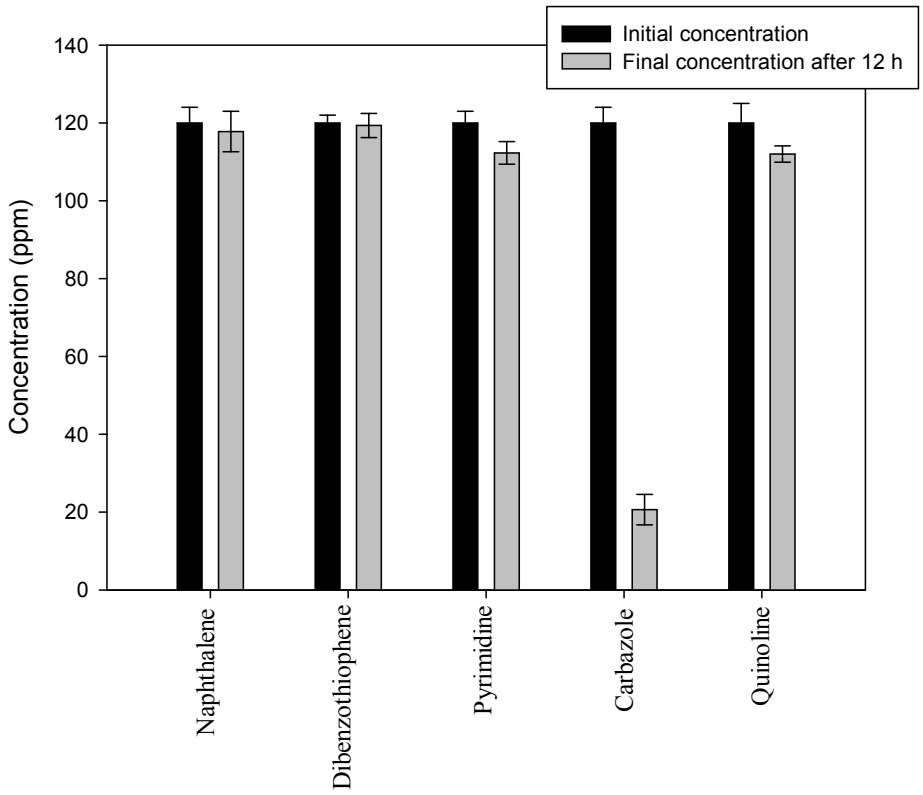


Fig S8. Adsorption selectivity of carbazole using carbazole-imprinted microspheres.

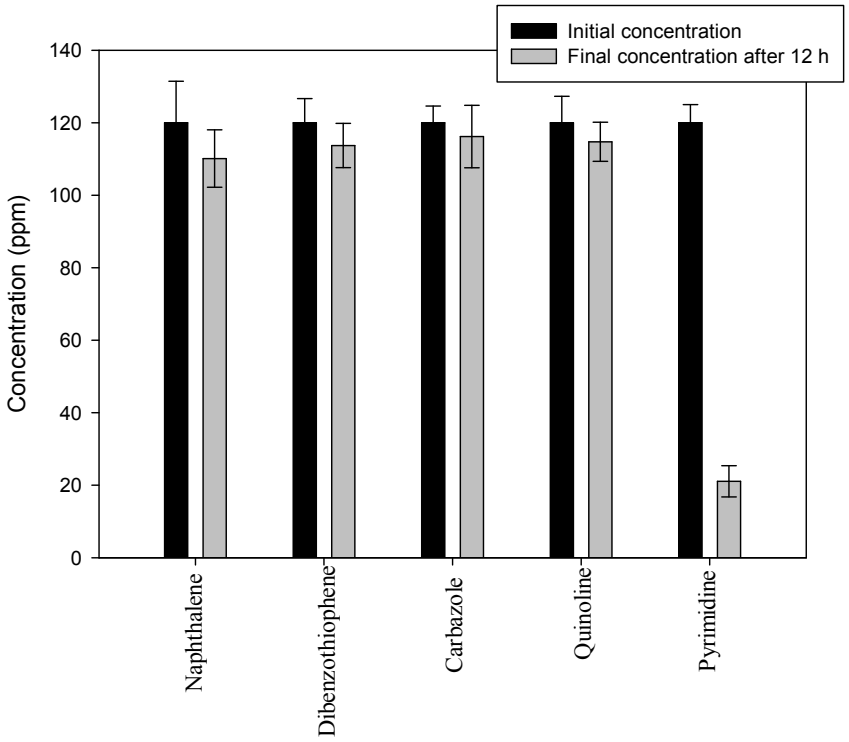


Fig S9. Adsorption selectivity of pyrimidine using pyrimidine-imprinted microspheres.

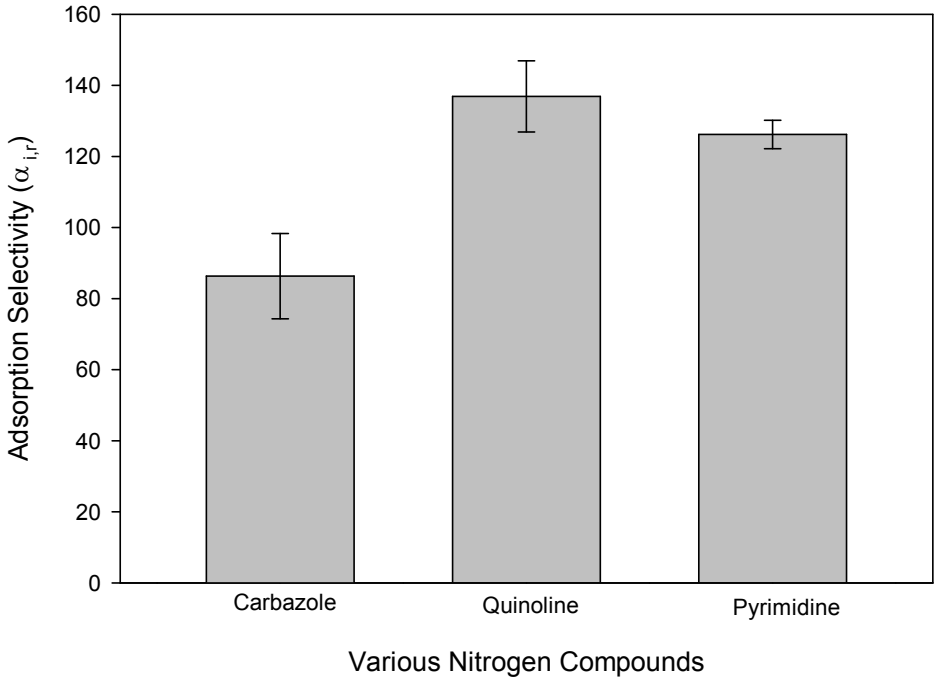


Fig. S10. Adsorption selectivity of imprinted microspheres (MIPs) after 5 h adsorption time.

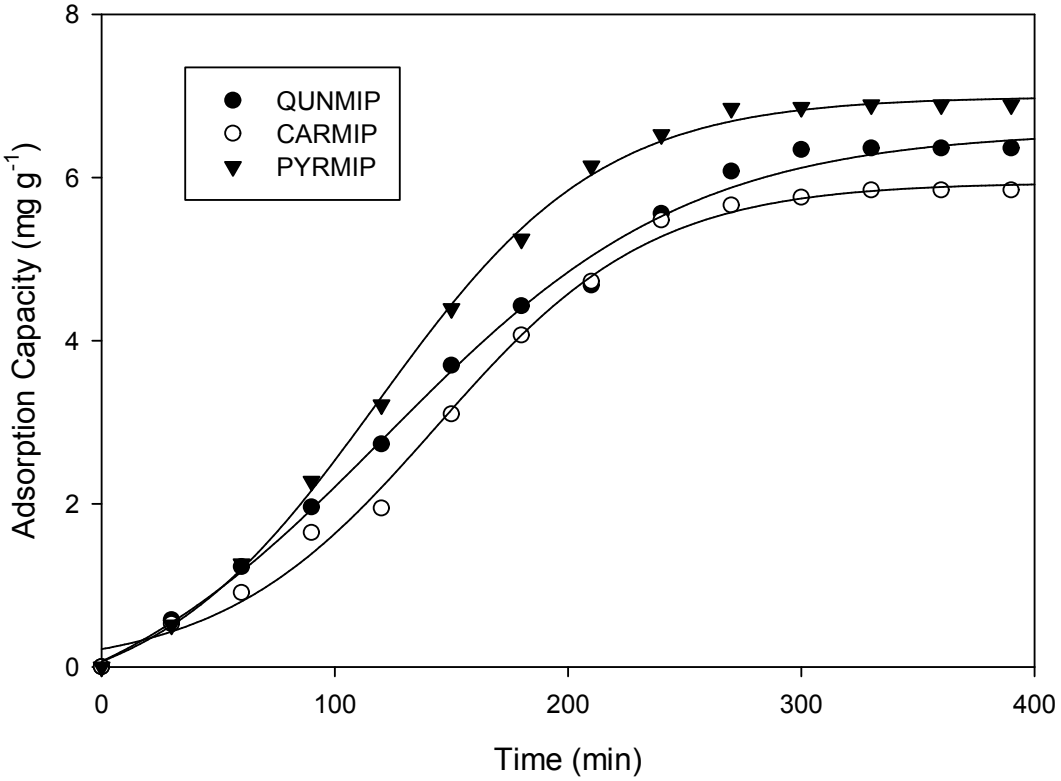


Fig S11. Kinetic of adsorption of the various nitrogen compounds over imprinted microspheres.

Table S1. Imprinting factor microspheres

Adsorbents	Qe (NIP)	Qe (MIP)	Imprinting Factor (k)
Pyrimidine	0.2	6.3	26.3
Quinoline	0.3	6.8	21.9
Carbazole	0.4	5.8	16.6

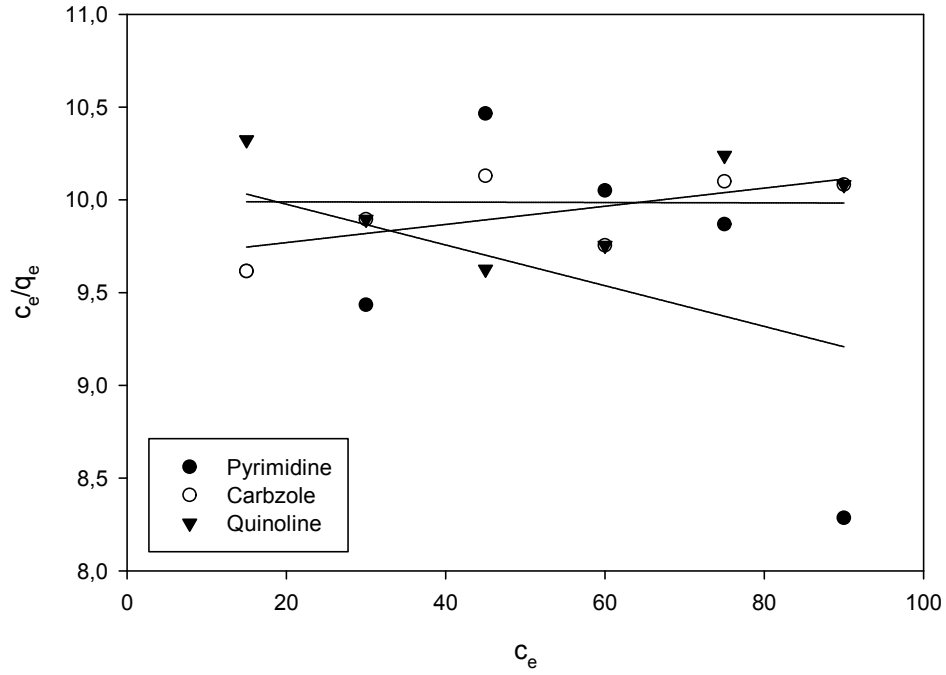


Fig. S12. Langmuir plot for (A) carbazole, (B) quinoline and (C) pyrimidine.

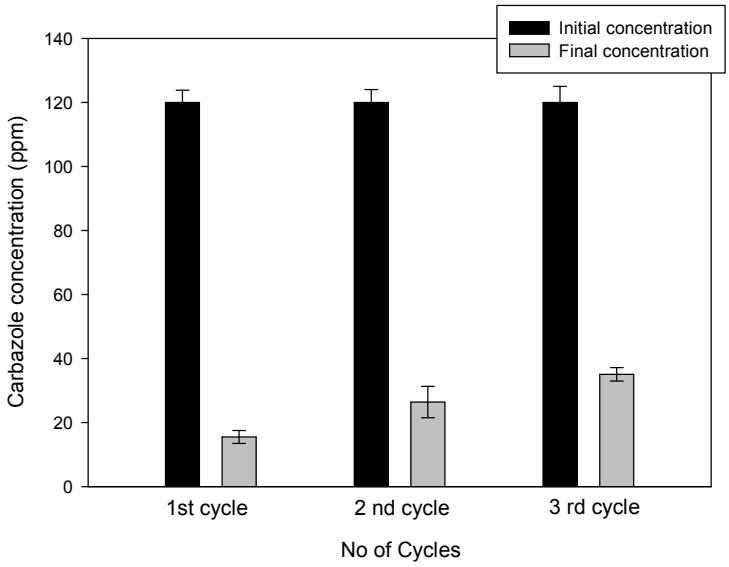


Fig. S13. Reusability studies on the use of carbazole-imprinted microspheres for the adsorption of carbazole.

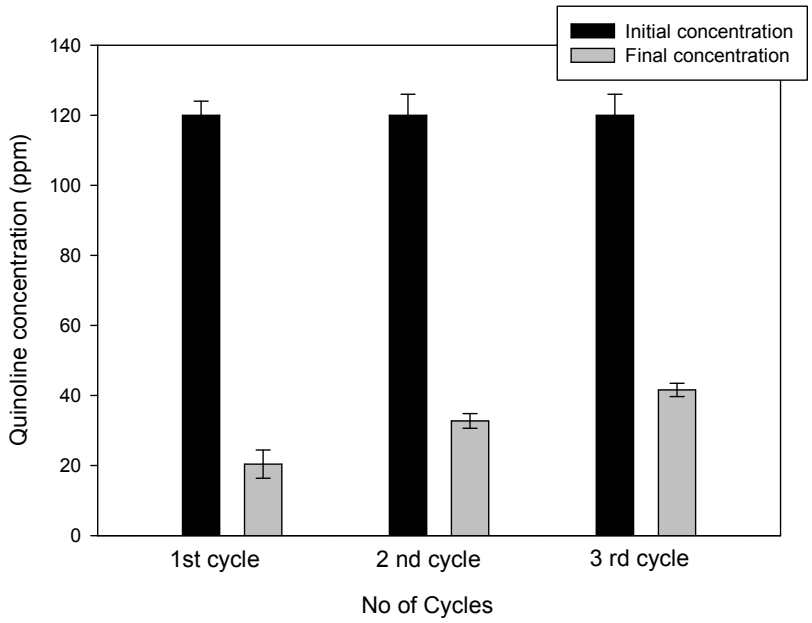


Fig. S14. Reusability studies on the use of quinoline-imprinted microspheres for the adsorption of quinoline.

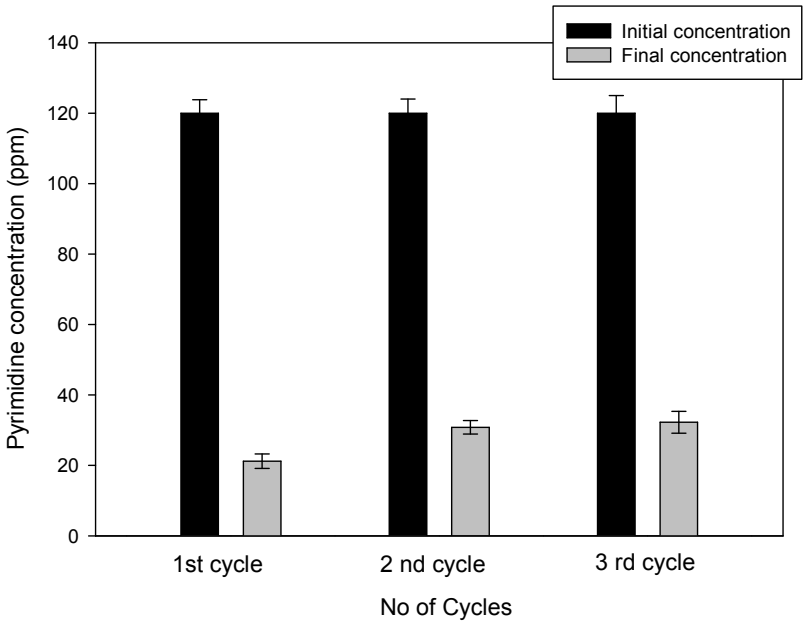


Fig. S15. Reusability studies on the use of pyrimidine-imprinted microspheres for the adsorption of pyrimidine.

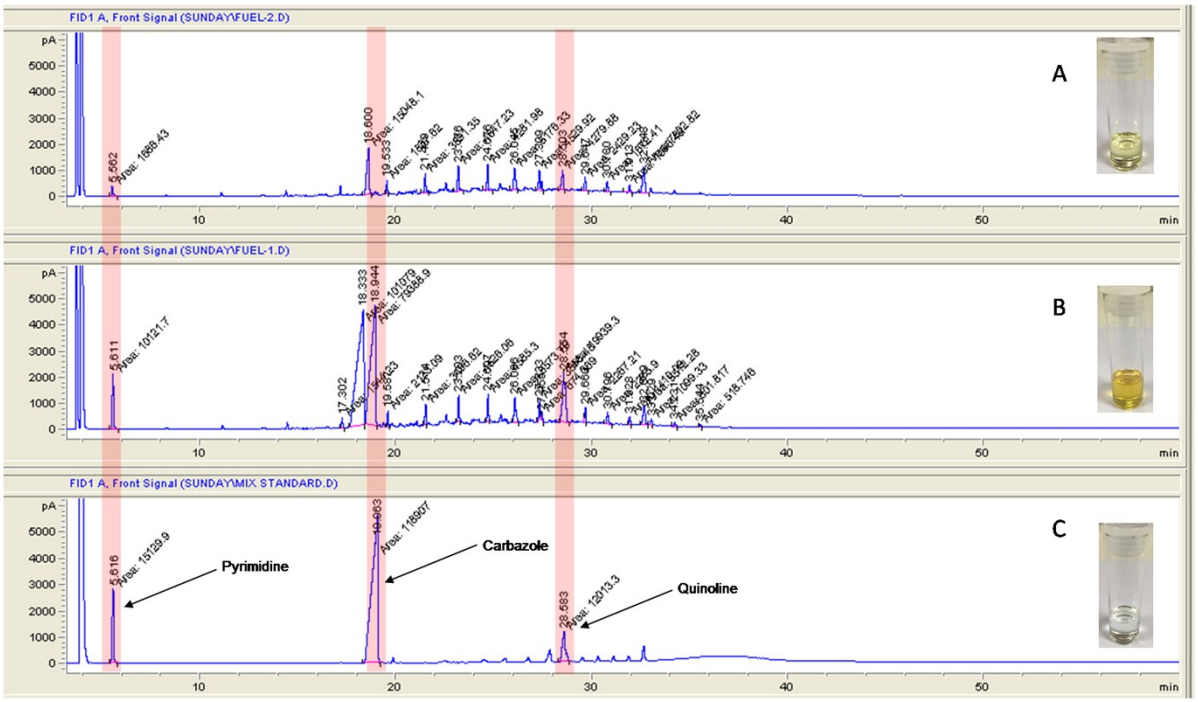
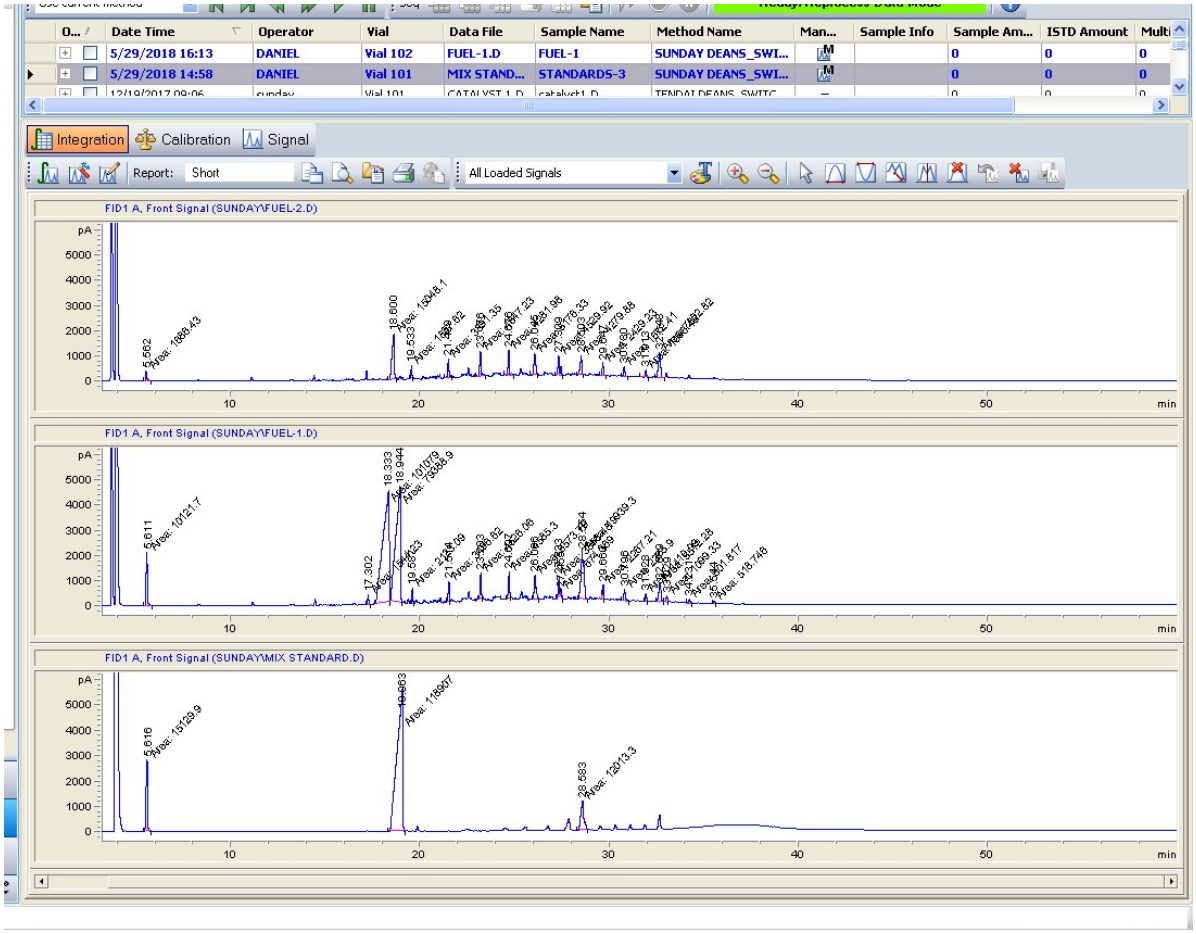


Fig. S16. GC-FID chromatograms of (A) diesel fuel after MIPs removal; (B) diesel fuel containing target nitrogen containing compounds before applying MIPs and (C) target nitrogen containing compounds (Inset: images of the fuel).

Conditions: Agilent 7890A gas chromatograph fitted with flame ionization detector (GC-FID). Column: DB 5 (30 m x 0.25 mm x 0.25 um); Inlet temperature: 250˚C; Carrier Gas and flow rate: Helium at 20 cm/s; Make-Up Gas and flow rate: Nitrogen at 30 mL/min; Split Ratio: 100:1; Column Temperature profile: Hold at 100˚C for 5 minutes. Ramp to 240C at 5˚C/min. Hold at 240˚C for 30 min.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Operator
Vial
Data File
Sample Name
Method Name
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5/29/2018 14:58
DANIEL
Vial 101
MIX STAND...
STANDARDS-3
SUNDAY DEANS_SWI...
Integration
Calibration
Signal
Report:
Short
All Loaded Signals
FID1 A, Front Signal (SUNDAY\FUEL-2.D)
FID1 A, Front Signal (SUNDAY\FUEL-1.D)
FID1 A, Front Signal (SUNDAY\MIX STANDARD.D)
pA
min

View 2