CONNECTING THE DOTS TO INNOVATION

ADSORPTIVE REMOVAL OF MUNITIONS COMPOUNDS FROM AQUEOUS SOLUTIONS VIA GRAPHENE NANOPLATELETS

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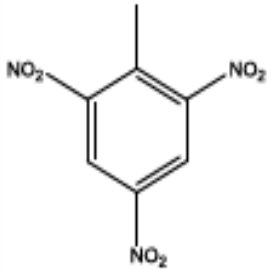
MOTIVATION

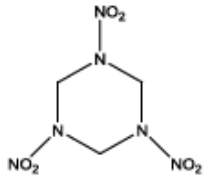
- Insensitive munitions (IM) are being evaluated as solutions to provide improved safety relative to legacy munitions
  - Reduced tendency for accidental or sympathetic detonation
- Knowledge gaps remain regarding environmental sustainability
  - Treatment and disposal techniques at facilities and ranges
- Current treatment technologies can be relatively inefficient
  - Relatively high mass loading of granular activated carbon (GAC) associated with high aqueous solubilities of compounds
  - Chemical treatment techniques provide unknown or potentially toxic products
- Other treatment and disposal techniques should be considered
  - Graphene is an emerging technology that has exhibited high efficacy for treatment

MUNITIONS COMPOUNDS

Legacy Munitions

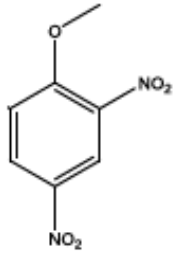


2,4,6-trinitrotoluene (TNT)

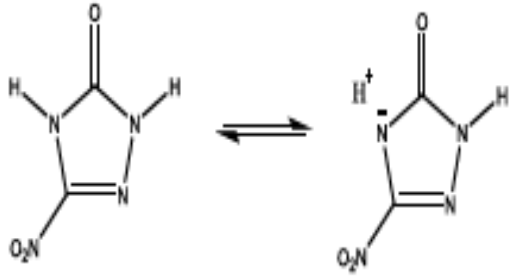


Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)

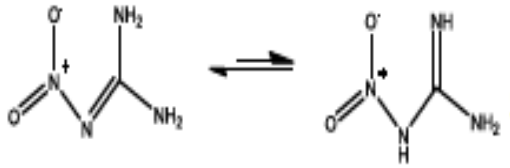
Insensitive Munitions



2,4-dinitroanisole (DNAN)



Nitrotriazolone (NTO)



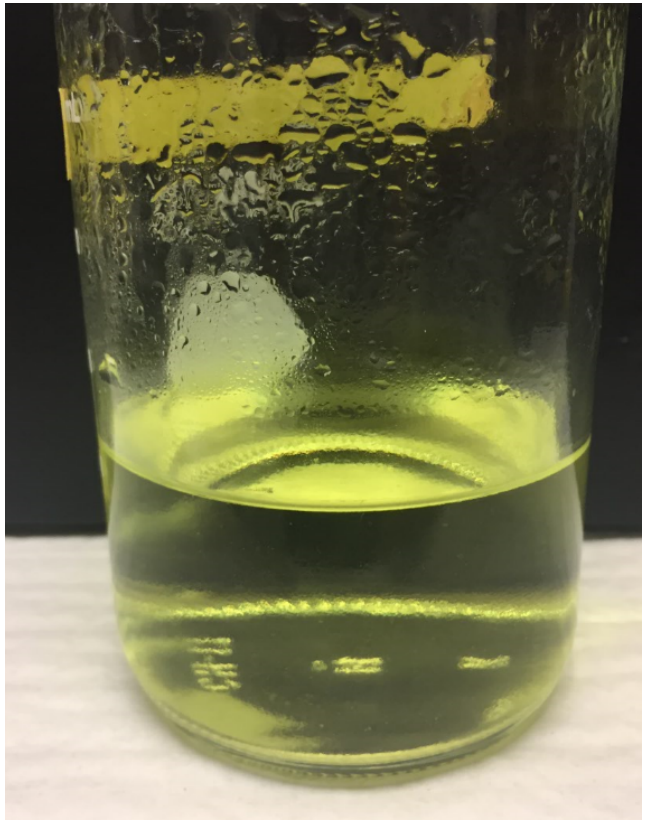
Nitroguanidine (NQ)

- Insensitive munitions (IMs) are currently being evaluated as alternatives to traditional munitions
- Pursuant to improvements in soldier safety via prevention of sympathetic detonation

IM PROPERTIES

Compound	Aqueous Solubility (mg/L)
NTO	12,800 (19 ºC)
NQ	4,100 (26 ºC)
DNAN	280 (25 ºC)
TNT	130 (20 ºC)
RDX	43 (25 ºC)

pK_{a1} of NTO = 3.76[a]
pK_{a2} of NTO = 11.25[b]



Aqueous Solution Containing NTO

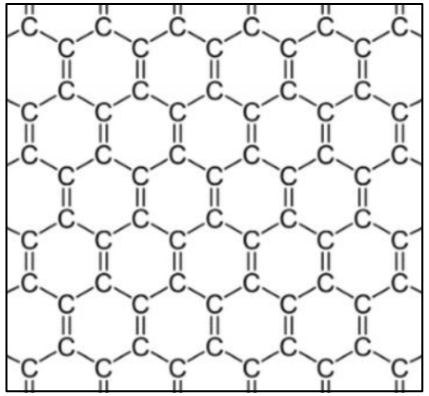
MUNITION-LADEN WATER

- Environmental concerns for IM formulations
  - Room temperature solubility of certain compounds exceeds 200x those of traditional formulations
  - Coloration of water upon dissolution of certain compounds
    - NTO: yellow
    - Legacy munitions: Pink water
  - Acidification by NTO

- Treatment strategies
  - Complex removal systems specific to individual compounds
  - Destructive technologies
    - Toxic or unknown byproducts
  - Adsorptive technologies
    - Traditional technologies are inefficient for all IM and legacy compounds

GRAPHENE

- Graphene is a 2-D carbon nanomaterial
  - Single-layer graphite
- Uses
  - Environmental treatment
  - Mechanical property enhancement
- Disperse-able within other matrices
  - Polymer matrices
  - Cement



Graphene[#a]

Graphene-reinforced Concrete[#b]

Polymer Composite

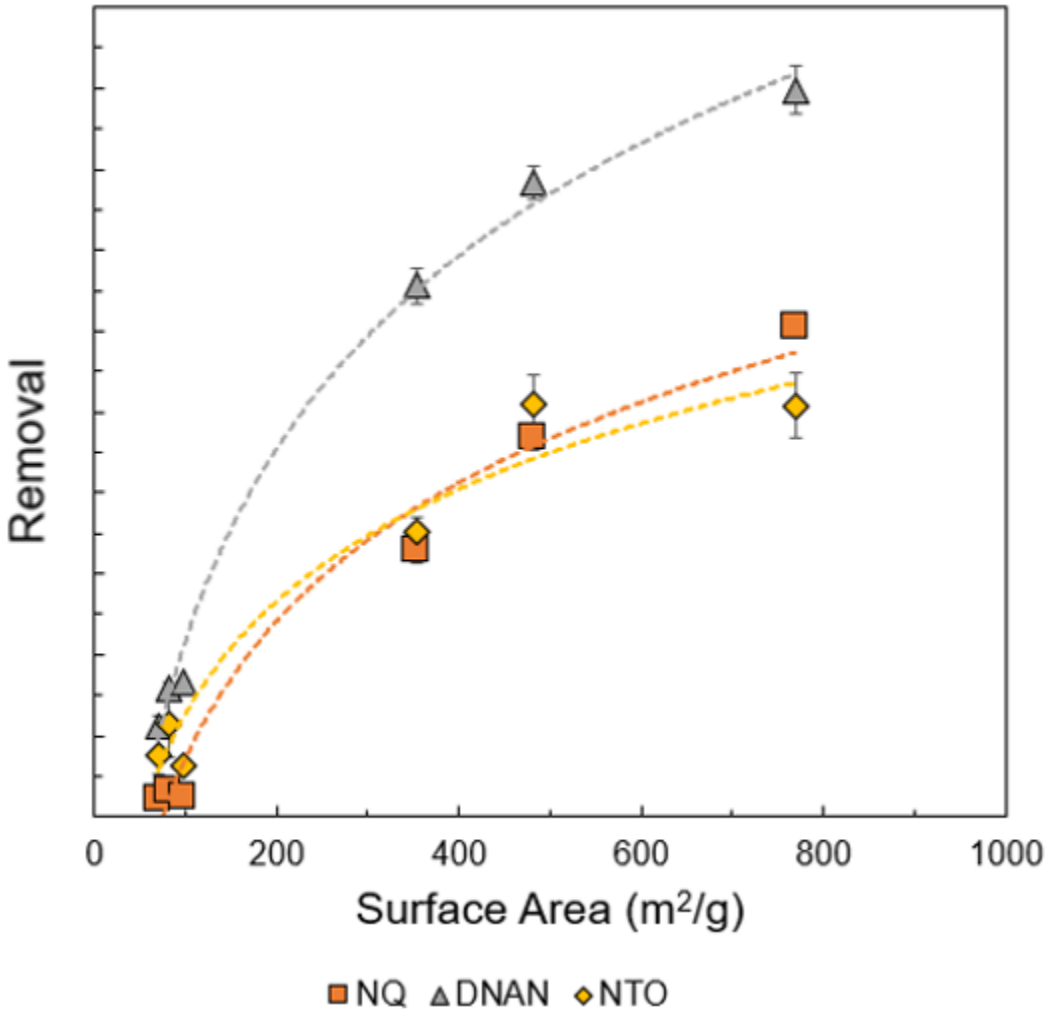
(a)https://www.graphene-info.com/graphene-structure-and-shape
(b)https://www.dezeen.com/2018/05/03/graphene-reinforced-concrete-stronger-university-of-exeter-scientists/

APPROACH

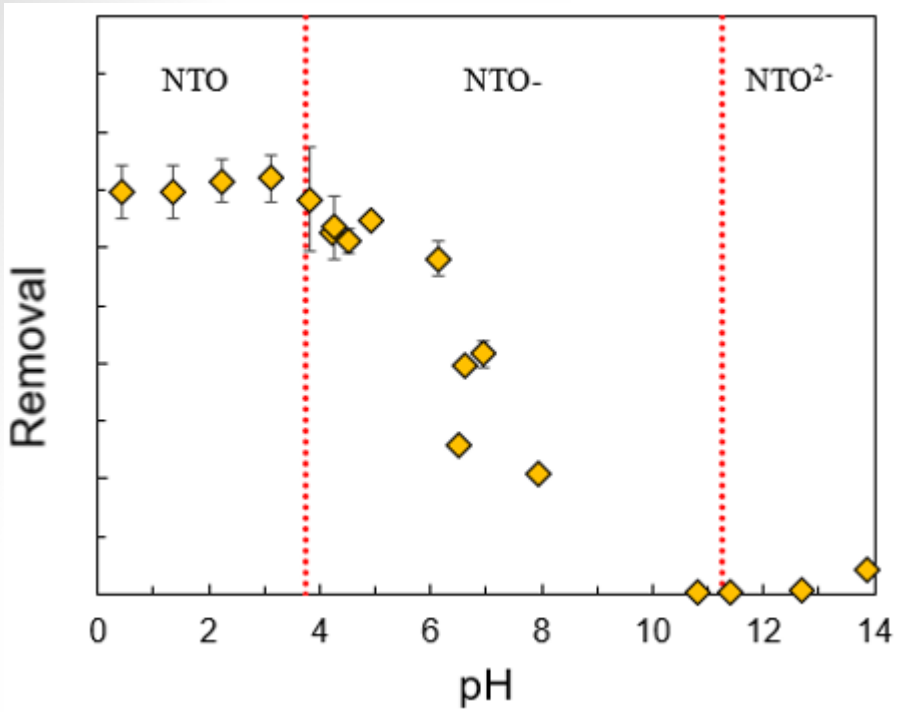
- Three IM compounds were studied
  - NTO, DNAN, and NQ
- Adsorption experiments with graphene nanoplatelets (GnP)
  - Dependence on the following:
    - Surface area
    - Ionic strength (IS)
    - pH
    - Time
    - Dose
- Modeling of adsorption
  - Isotherms
  - Kinetics
- Comparison against granular activated carbon (GAC)

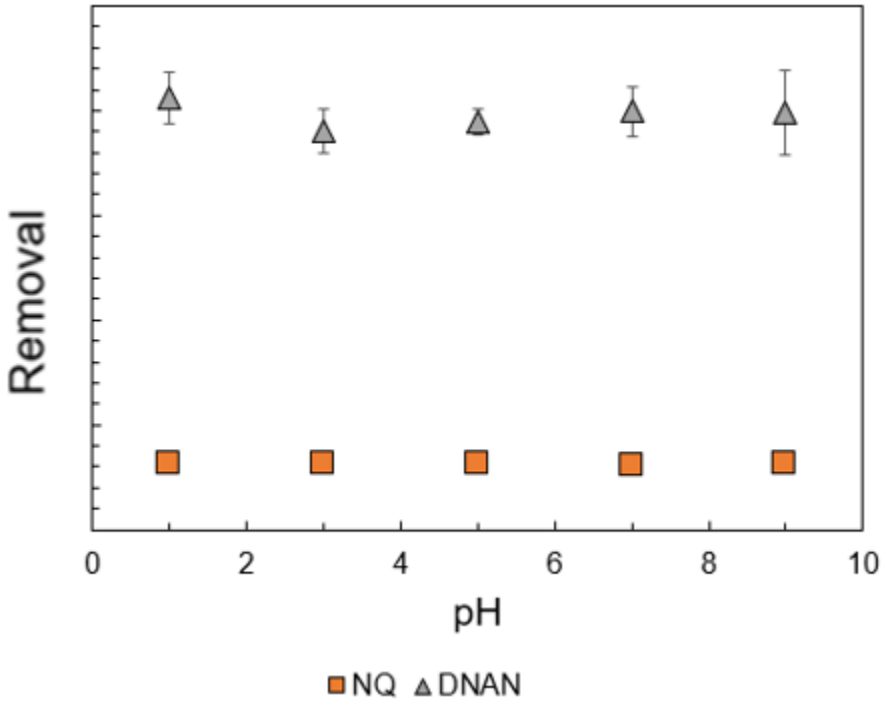
SURFACE AREA IMPACTS ON ADSORPTION

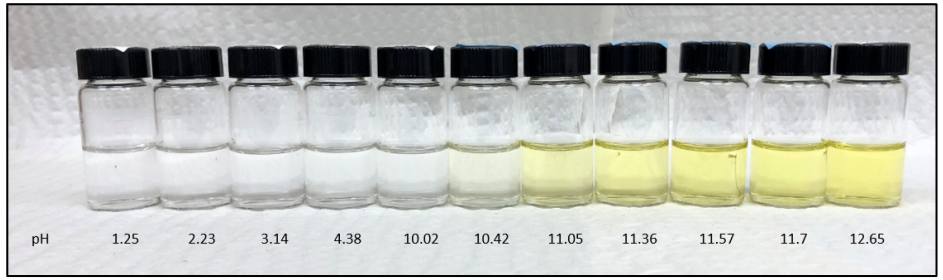
- Different GnP grades evaluated
- Higher surface area provided greater removal performance
- Logarithmic trend likely related to reduction in driving force as aqueous concentration decreased throughout adsorption process



pH IMPACTS

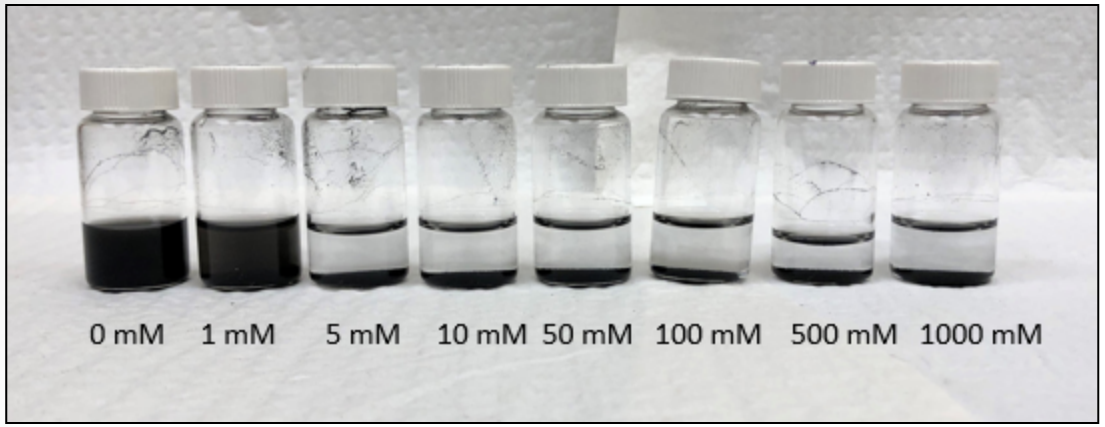


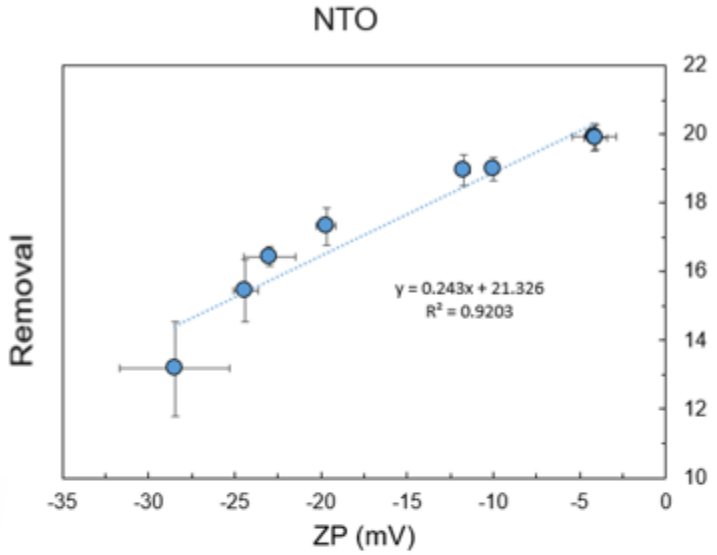


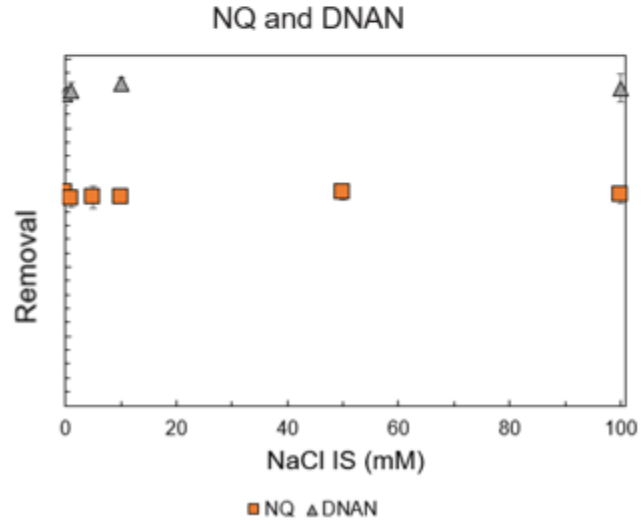


- NTO removal decreased as pH increased
  - Electrostatic repulsion
- DNAN or NQ adsorption was not impacted by pH

IONIC STRENGTH IMPACTS

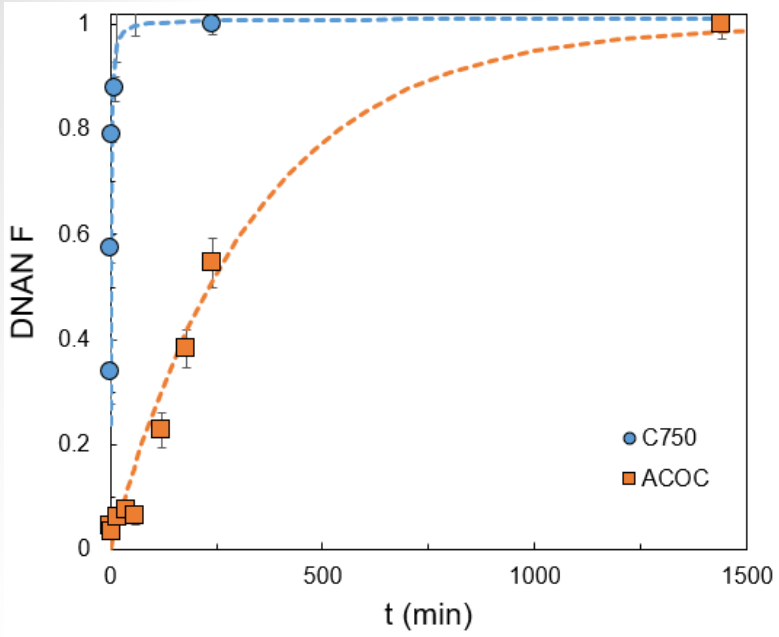


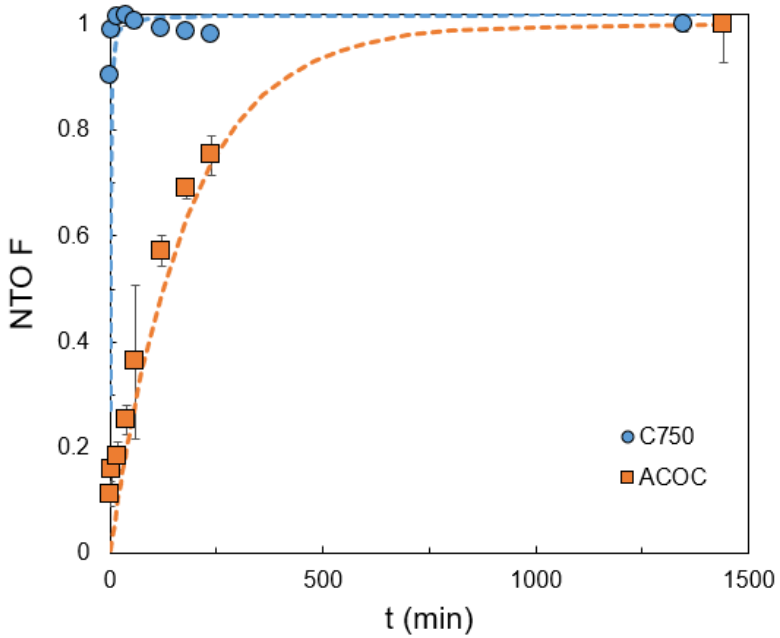


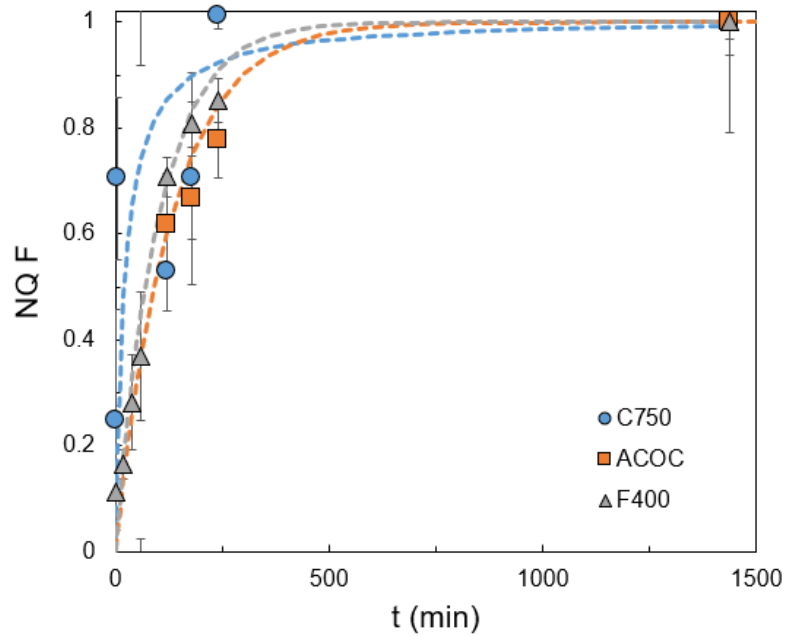


- As ionic strength was increased, ZP decreased.
- Settling of GnPs was observed as ionic strength exceeded 5 mM.

ADSORPTION KINETICS



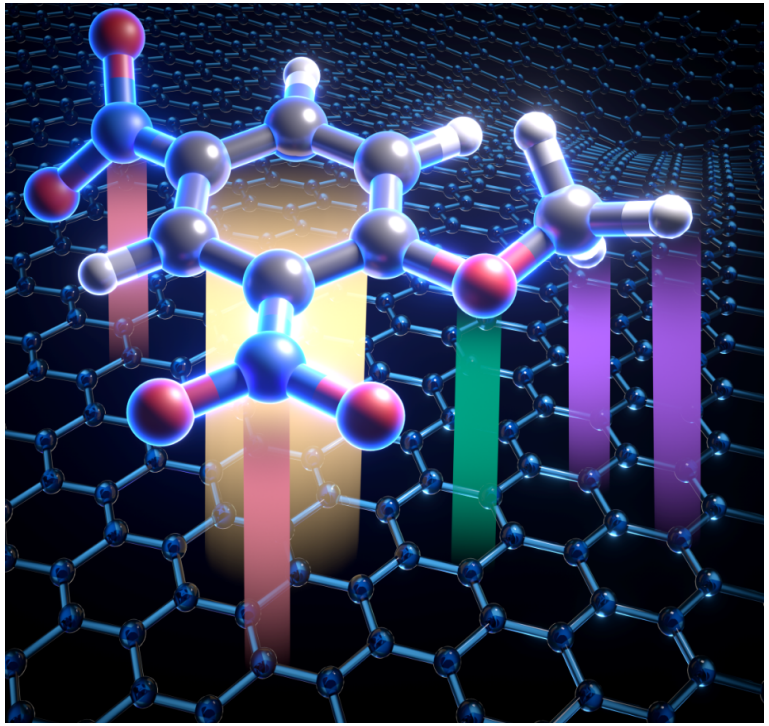


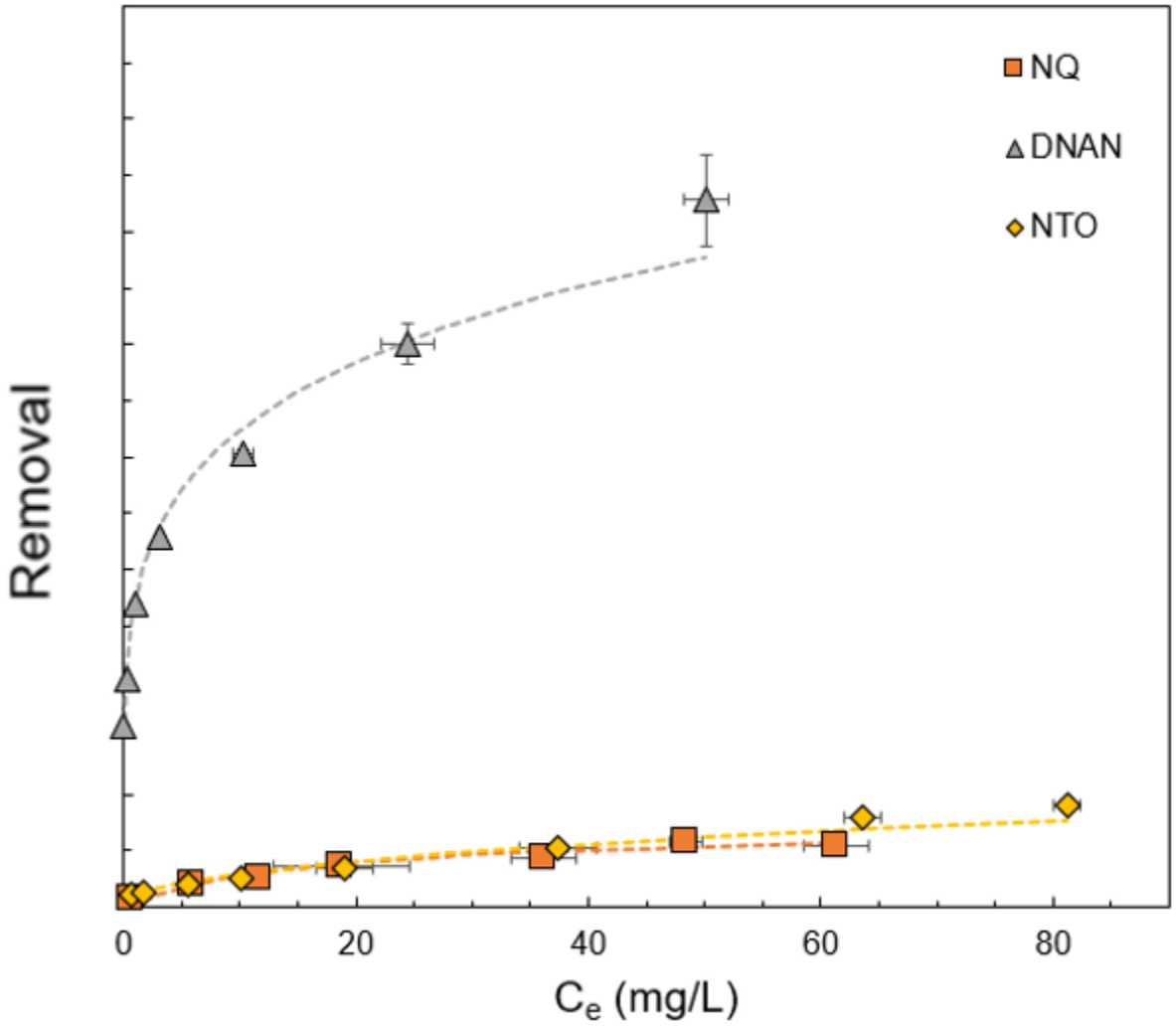


- GnPs provided more rapid adsorption kinetics compared to GAC
  - Performance gap seemed to close at MW decreased

ISOTHERMS

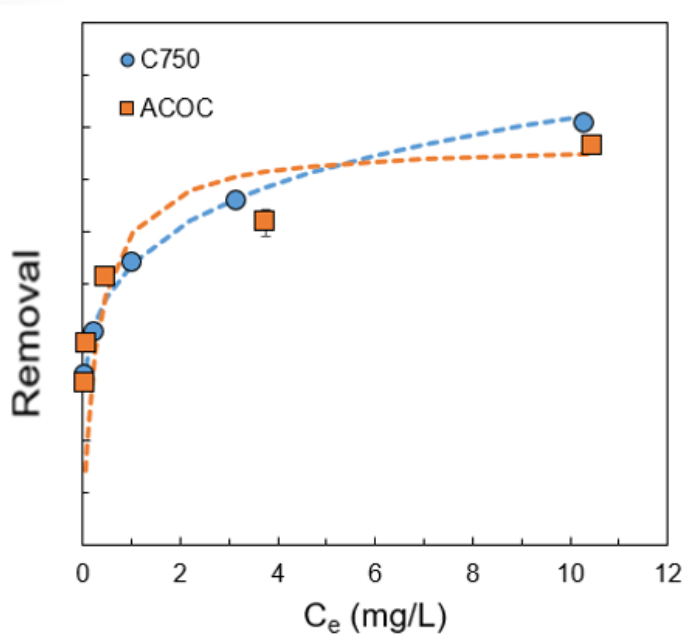
- DNAN removed with highest capacity
- Mechanisms:
  - π-π interactions (DNAN)
  - Van der Waals forces (all)



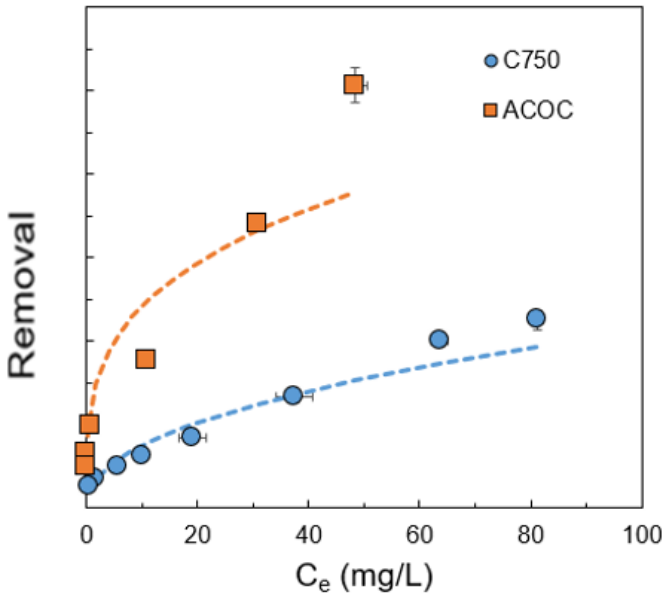


COMPARATIVE ISOTHERMS

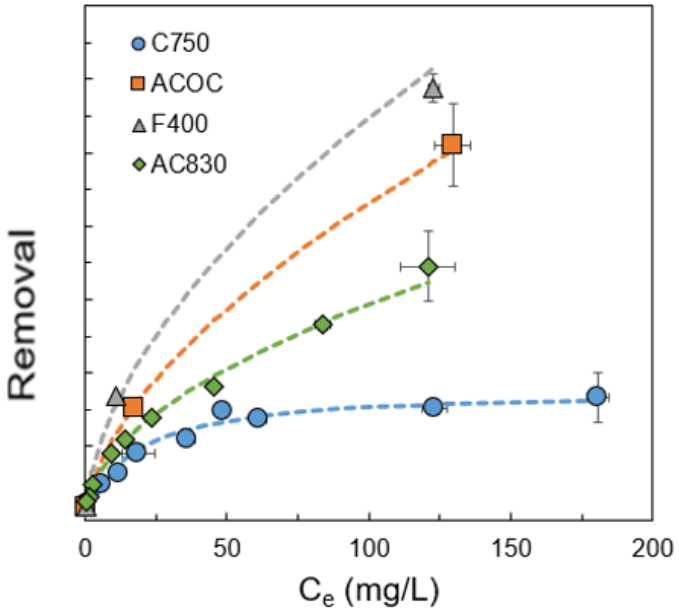
DNAN



NTO



NQ



CONCLUSIONS

- GnPs are capable of rapidly removing IM compounds from aqueous solutions
- DNAN adsorption is likely promoted by π-π interactions that enhance removal performance
- Electrostatic repulsion occurs at neutral pH between NTO and GnP, hindering removal
- Surface area contributes greatly to adsorption of IM

ACKNOWLEDGEMENTS

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QUESTIONS?

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