Challenges in Managing Mercury in Field Development and Production

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Heteroligand Gold Nanoprobes: A Plasmonic Approach to Mercury Ion Sensing

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Introduction

- Current mercury measurement and detection for water quality monitoring requires laborious sampling and timely analysis, e.g. tedious digestion and preparation steps prior to analysis.
- Often, the concentration reported via analysis gives low value, yet extensive resources were used.
- Thus, gold nanoparticle combined with peptide offers instantaneous mercury detection in water for operators via a simple "Mercury screening kit" to indicate its presence.

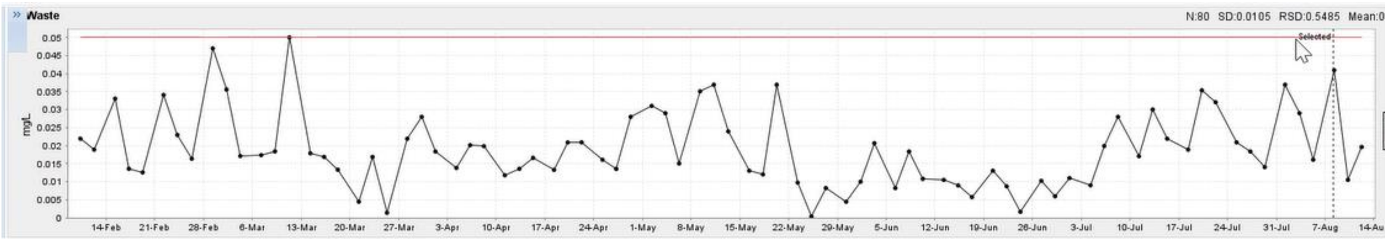


Figure 1: Sample of current mercury measurement in industrial wastewater

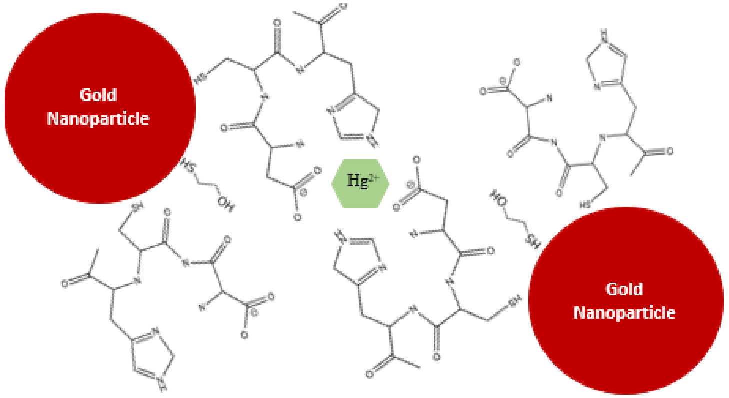


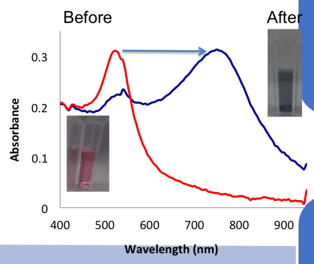
Figure 2: Illustration on aggregation of ligands on gold nanoparticles to Hg^{2+}

Methodology

Tripeptide Design and Selection

Tripeptide Solution Preparation

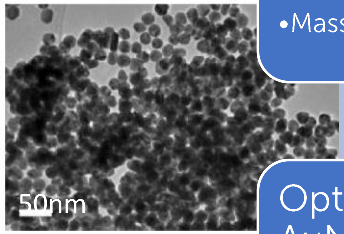
Tripeptides-AuNPs Preparation



Semi-Quantitative Screening of Tripeptide-AunPs

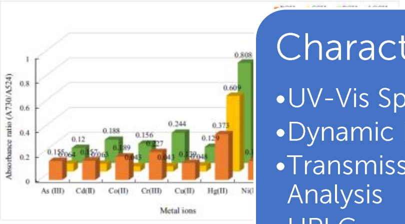
Optimization of Tripeptide-AuNPs

- pH
- Concentration

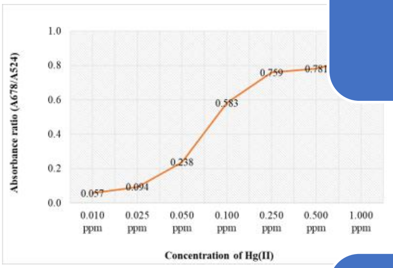


Characterization of AuNP:

- UV-Vis Spectra Analysis
- Dynamic Light Scattering Analysis
- Transmission Electron Microscope Analysis
- HPLC
- Mass Spectrometry



Validation of standard curve

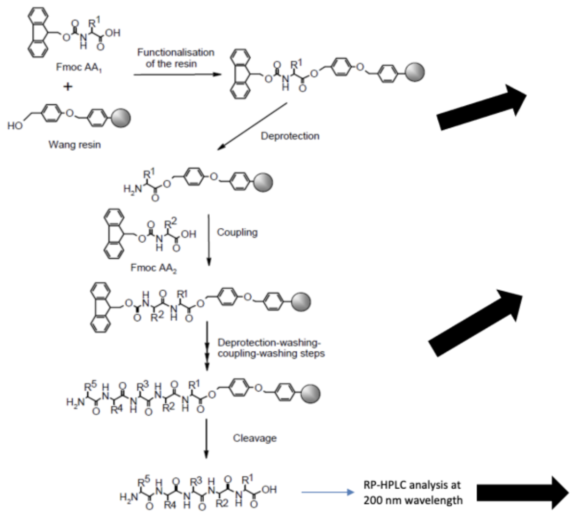


Testing on actual sample

Tripeptide Selection

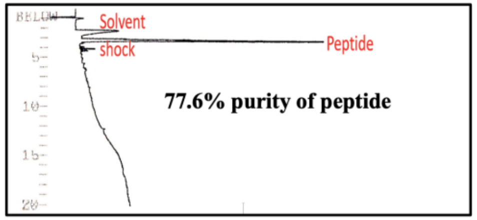
- 11 novel tripeptides were selected as ligands for the gold nanoparticle sensor from 169 peptides model – target purity of 95-99% using solid phase peptide synthesis method.
- Verification of the purity and the peptide grade (based on molecular weight) determined via HPLC & MS Spectroscopy.

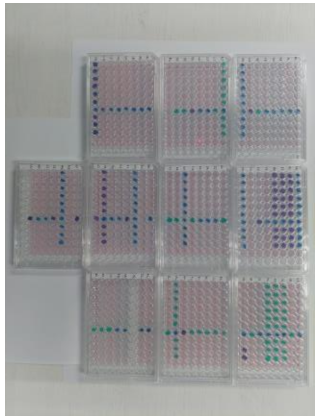
Solid phase peptide synthesis (HCH)



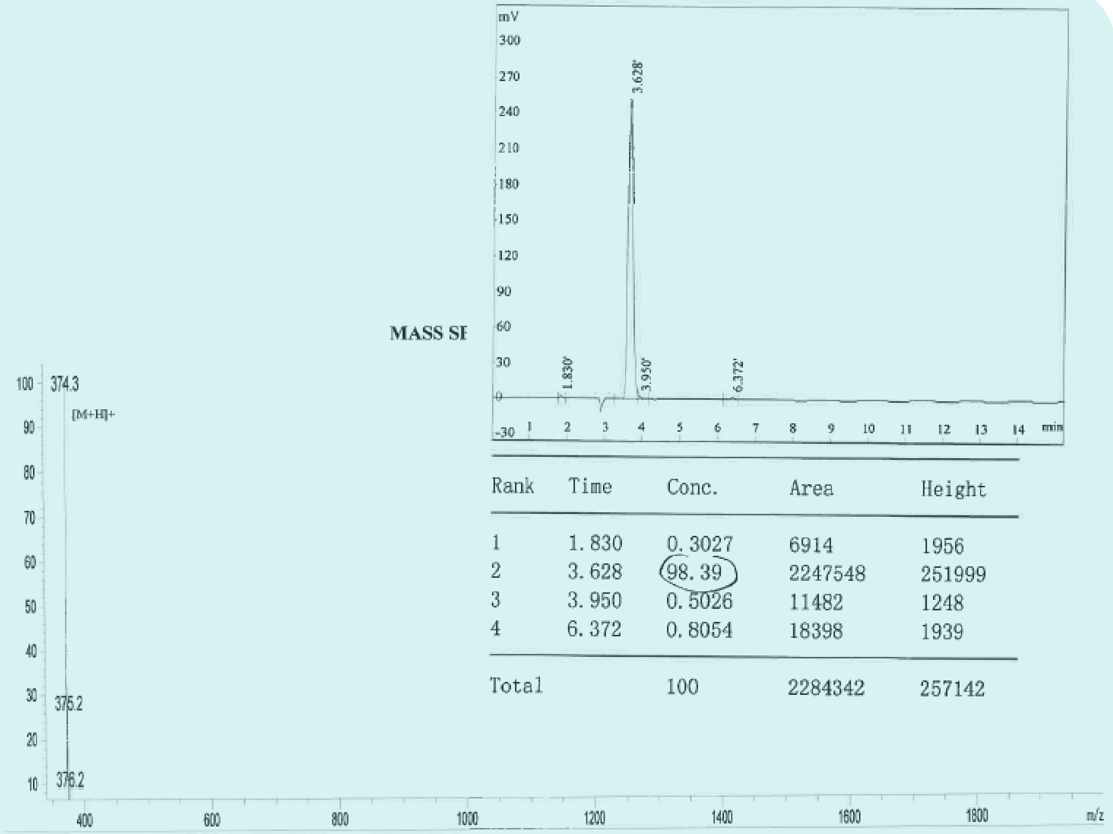
- Loading rate determination
- 1st % loading rate was 50.7%
- Final % loading rate was 48.0 %

- Peptide yield = 99.8 mg





- Design of AuNP-peptide library constructed for mercury detection
- Limitation – screening done via naked eye observation, potential improvement via microplate reader.



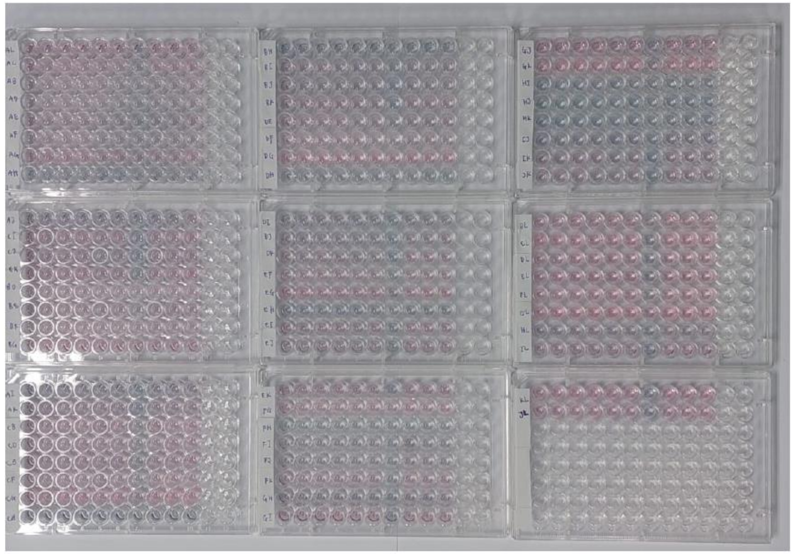
Rank	Time	Conc.	Area	Height
1	1.830	0.3027	6914	1956
2	3.628	98.39	2247548	251999
3	3.950	0.5026	11482	1248
4	6.372	0.8054	18398	1939
Total		100	2284342	257142

Sample Description
Analyzed date: 2020-09-14
Analyst: YU
Sample: DCH DH-3
M.W.: 373.38
Lot. No.: P200901-XF354439

Instrument: Agilent-6125B
Probe: ESI
Nebulizer Gas Flow: 1.5L/min
CDL: -20.0v
CDL Temp.: 250 °C
Block Temp.: 200 °C

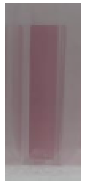
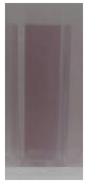
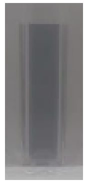
Probe Bias: +4.5kv
Detector: 1.5kv
T. Flow: 0.2ml/min
B. Conc.: 50%H2O/50%ACN

Semi Quantitative Screening



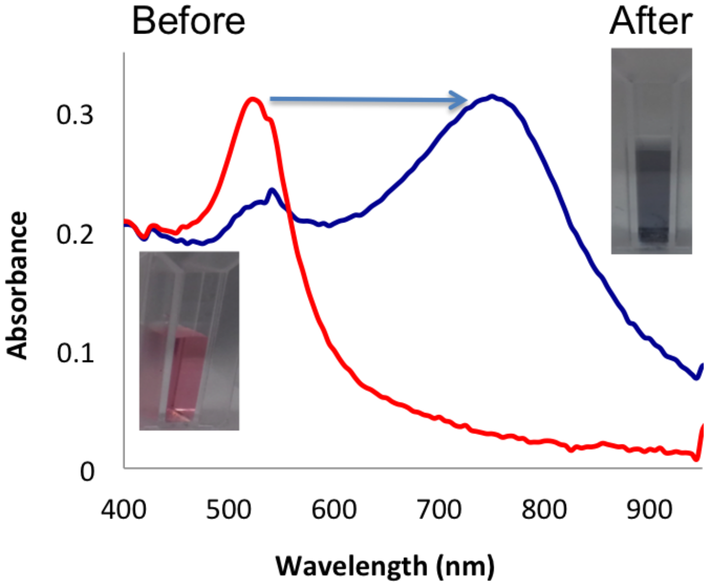
- Photo image of colorimetric semi quantitative screening. Addition of mercury will result in different colour changes

No.		Metal ions									
		As^{3+}	Cd^{2+}	Co^{2+}	Cu^{2+}	Cr^{3+}	Fe^{3+}	Hg^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}
MONOLIGAND											
1	PCH							+++			
2	NCH							++			
3	DCH							+			
4	MCH							+			
5	HCD							+			
6	HCM							+			
7	DCD										
8	MCM	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
9	QCW							+++			
10	QCF							++			
11	QCY							++			
12	GSH							++			
HETEROLIGAND											
13	PCH/GSH							+++			
14	PCH/NCH							+++			
15	PCH/DCH							+++			
16	PCH/MCH							+++			
17	PCH/HCD							+++			
18	PCH/HCM							++			
19	PCH/DCD										
20	PCH/MCM	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
21	PCH/QCW	++	++	++	++	++	++	+++	++	++	++
22	PCH/QCF	++	++	++	++	++	++	+++	++	++	++
23	PCH/QCY							+++			
24	NCH/GSH							+++			

Level of aggregation	25% aggregation	50% aggregation	100% aggregation
Photo-image			

- The level of aggregation was observed according to color ratings.
  - Low level (25% aggregation) = red-purple (+)
  - Mid level (50% aggregation) = purple (++)
  - High level (100% aggregation) = blue (+++)

Signal quantification



Gold nanoparticle interaction with tripeptide

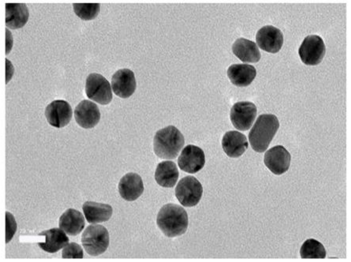
Tripeptide	Size particle (d. nm)	PdI	Zeta potential (mV)
Bare AuNPs	25.63 ± 0.59	0.201	-33.87 ± 2.48
PCH	71.93 ± 0.99	0.455	-27.90 ± 1.65
NCH	63.17 ± 1.87	0.544	-31.83 ± 0.99
DCH	24.98 ± 0.08	0.189	-39.37 ± 3.87
MCH	39.78 ± 1.07	0.564	-34.47 ± 1.05
HCD	25.90 ± 0.17	0.212	-32.80 ± 3.04
HCM	41.97 ± 2.16	0.442	-31.03 ± 3.31
DCD	28.73 ± 0.14	0.246	-36.23 ± 3.03
MCM	27.73 ± 0.33	0.38	-24.03 ± 2.33
QCF	25.36 ± 0.18	0.18	-30.53 ± 0.32
QCW	25.90 ± 0.17	0.22	-35.50 ± 2.55
QCY	25.42 ±0.34	0.19	-29.73± 2.57
GSH	25.78 ± 0.13	0.19	-34.27 ± 5.09

- Particle size, PdI & Zeta potential comparison from freshly prepared vs. addition of Hg^{2+} (n=3)

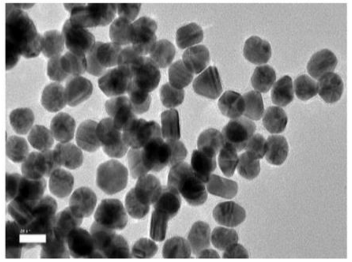
No.	Tripeptide-AuNPs (after addition of Hg^{2+})	Particle size (d.nm)	PdI	Zeta potential
1.	DCH-AuNPs	60.69±1.57	0.327	-20.03±0.35
2.	HCD-AuNPs	56.25±0.76	0.305	-20.83±0.95
3.	DCH/HCD- AuNPs	79.20±2.50	0.354	-17.53±1.15

- Particle size changes indicated the aggregation level
- Negative surface charge through zeta potential shows the ability to detect positively charged metal ions.
- DCH/HCD-AunP had the largest particle size and highest PdI value – highest uniformity of particle aggregation.
- Supported by TEM analysis – shown aggregation with Hg^{2+}

Before addition of Hg^{2+}



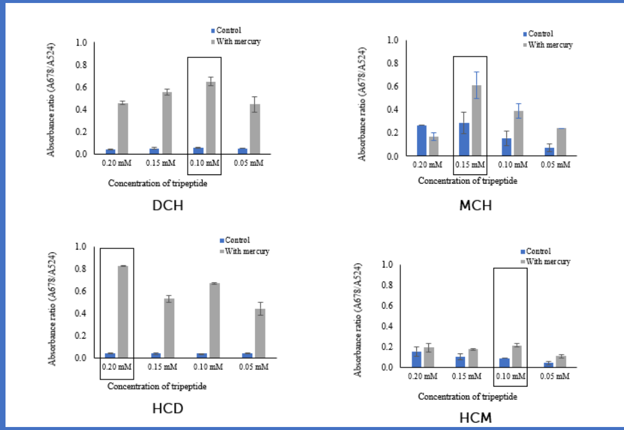
After addition of Hg^{2+}



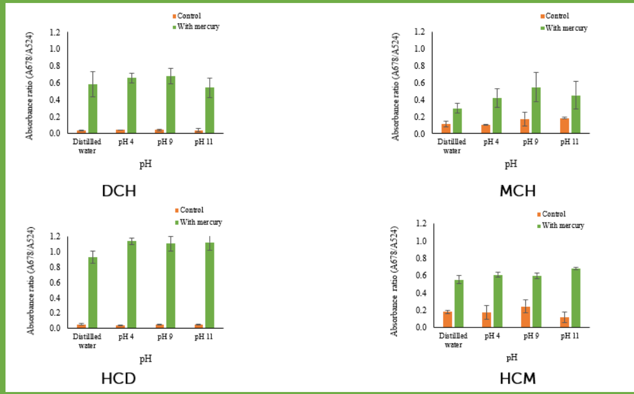
Surface chemistry optimisation & selectivity to Hg

- Target to find an optimum conditions to stabilize the tripeptide of choice conjugation onto the gold nanoparticle surface, thus enhance the sensing signal.
- Tripeptide candidates – HCD, DCH, MCH, HCM
- Mercury ion (Hg^{2+}) fixed for all conditions at 100 ppb.

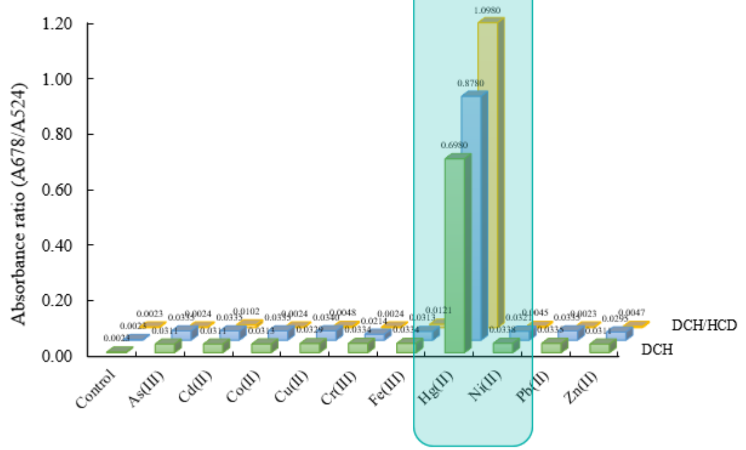
Varying peptide concentration



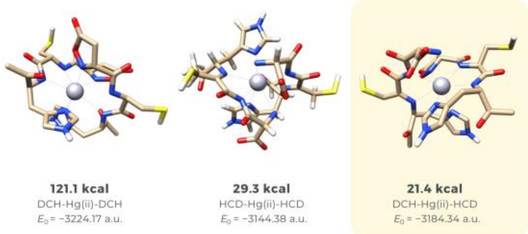
Varying pH

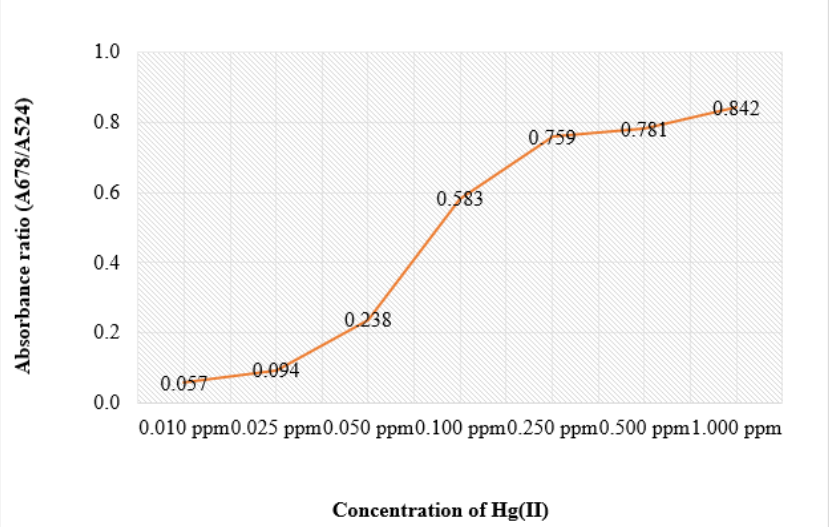


- Degree of aggregation (selectivity) for Hg is superior compared to other metals
- Sensitivity of DCH/HCD-AuNPs upon addition of 7 different concentration of Hg^{2+}

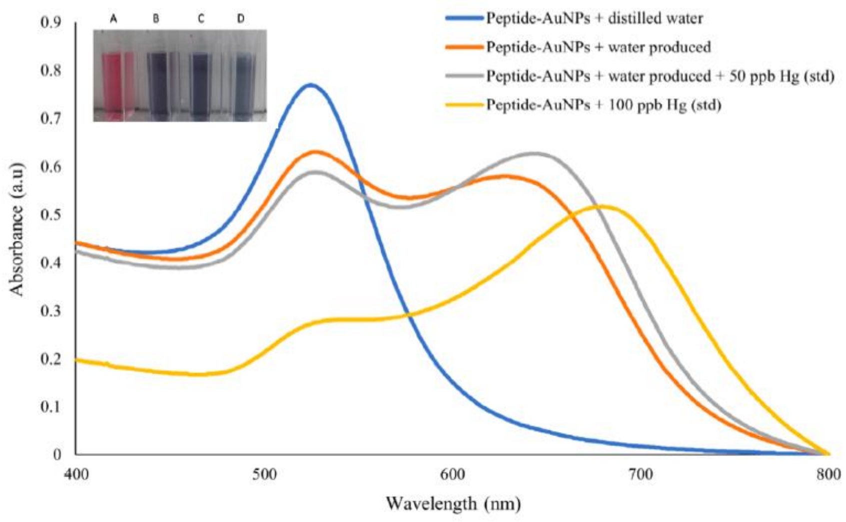


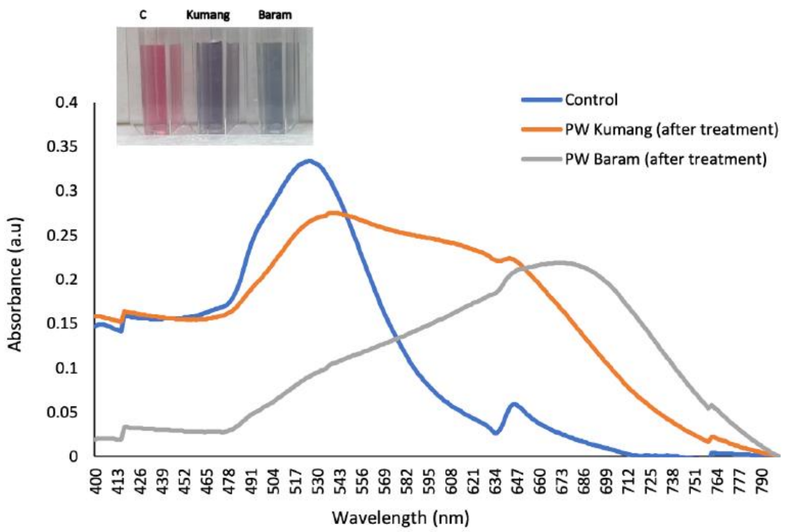
DFT (GAUSSIAN)





Validation with produced water





- Real samples were tested using DC/HD-AuNP as shown above gives qualitative indication of mercury spiked in the samples.
- More samples are required to verify the limitation of this nanoprobes.

Conclusion & Way forward

- Mercury presence via plasmonic detection is technically proven, however further investigation is required.
- Moving forward, the following could be further explored:
  - Field testing and validation
  - Sensor miniaturization and integration
  - Selectivity studies to evaluate other heavy metals.
  - Long-term stability and reusability