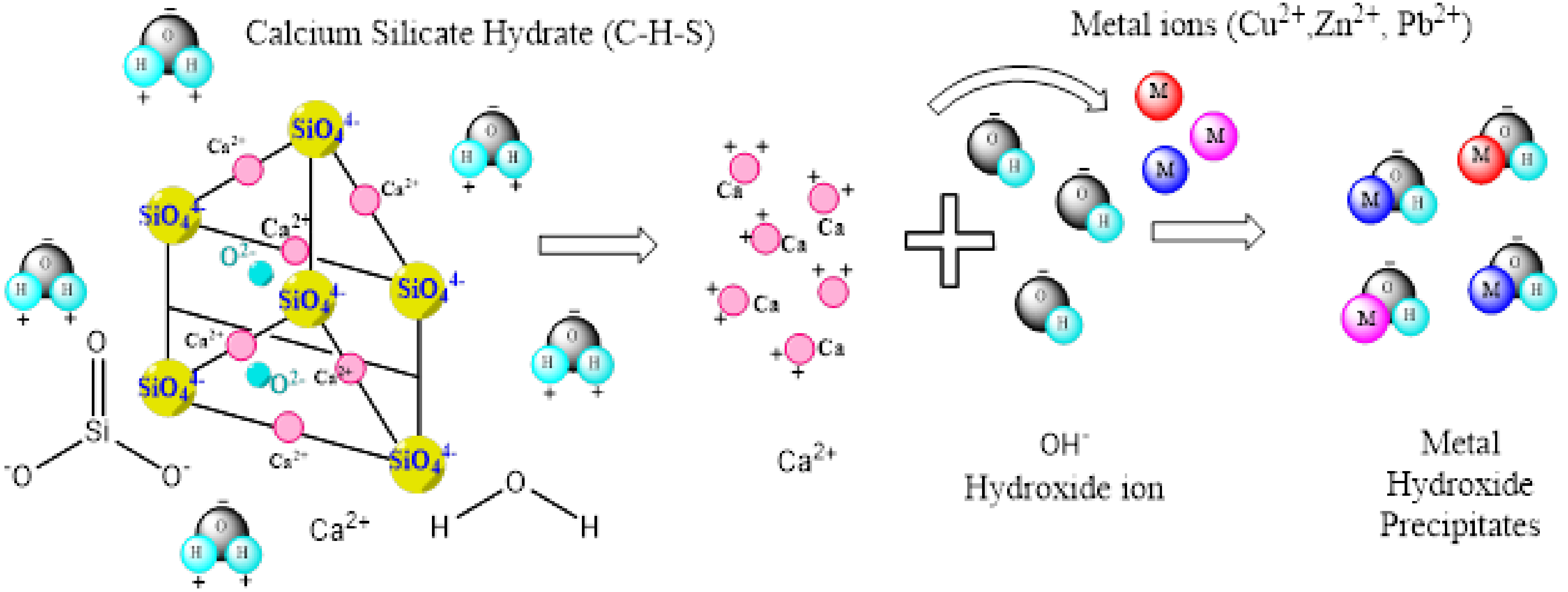
# Biochar admixture cement mortar fines for metal removal from water: a techno-economic feasibility study





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V4 Biochar Platform

**17 sept, 2021**

# Outline

Background

Rationale/The Drivers

Overarching Aim and Objectives

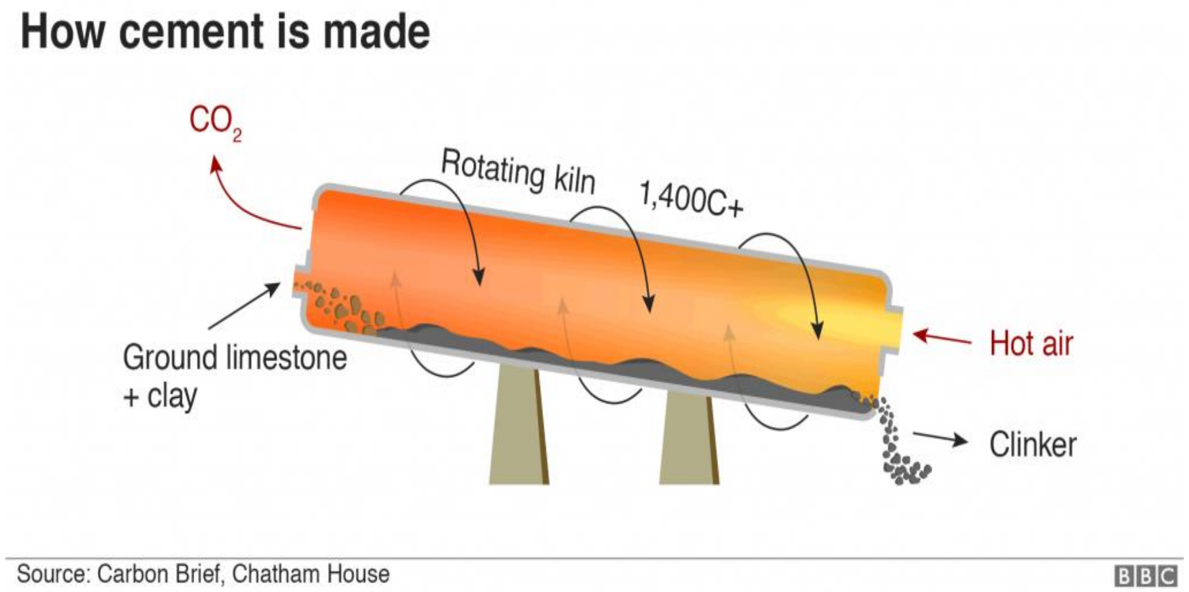
Materials & Method

Results and Discussions

Conclusions

# Background & Drivers

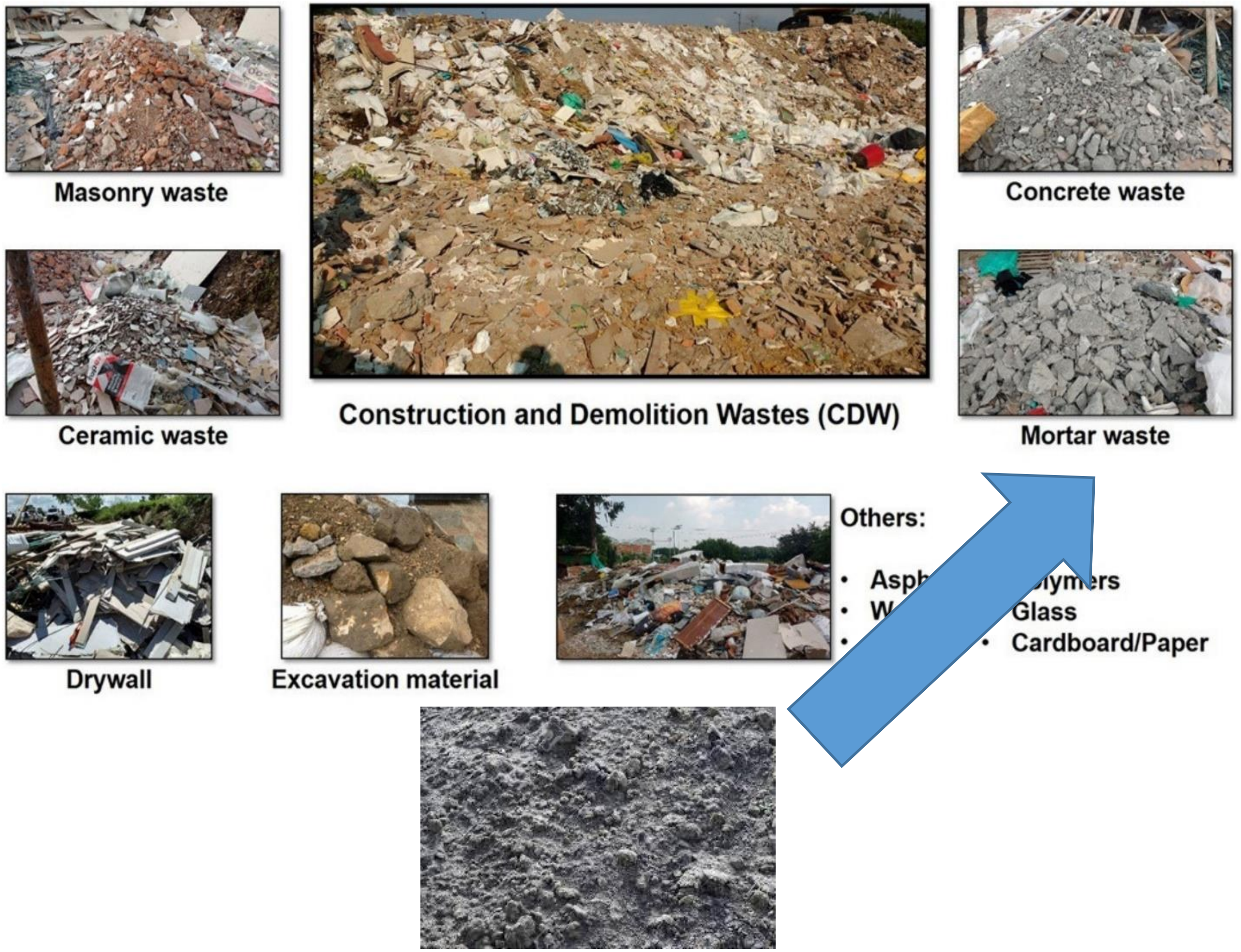
- The total amount of global Portland cement production in 2017 exceeds 4.0 billion metric tons (U.S.G.S)
- The amount of cement hydration products in hardened cement mortar is ~ 5 billion metric tons ***(~1.2 ton of water is needed for complete hydration of 1 ton cement)***
- Most of the hardened cement mortar converges into waste concrete once the buildings and concrete structures are demolished and abandoned




**The cement production process is responsible for 95% of concrete's carbon footprint**

# Background & drivers – Cont’d

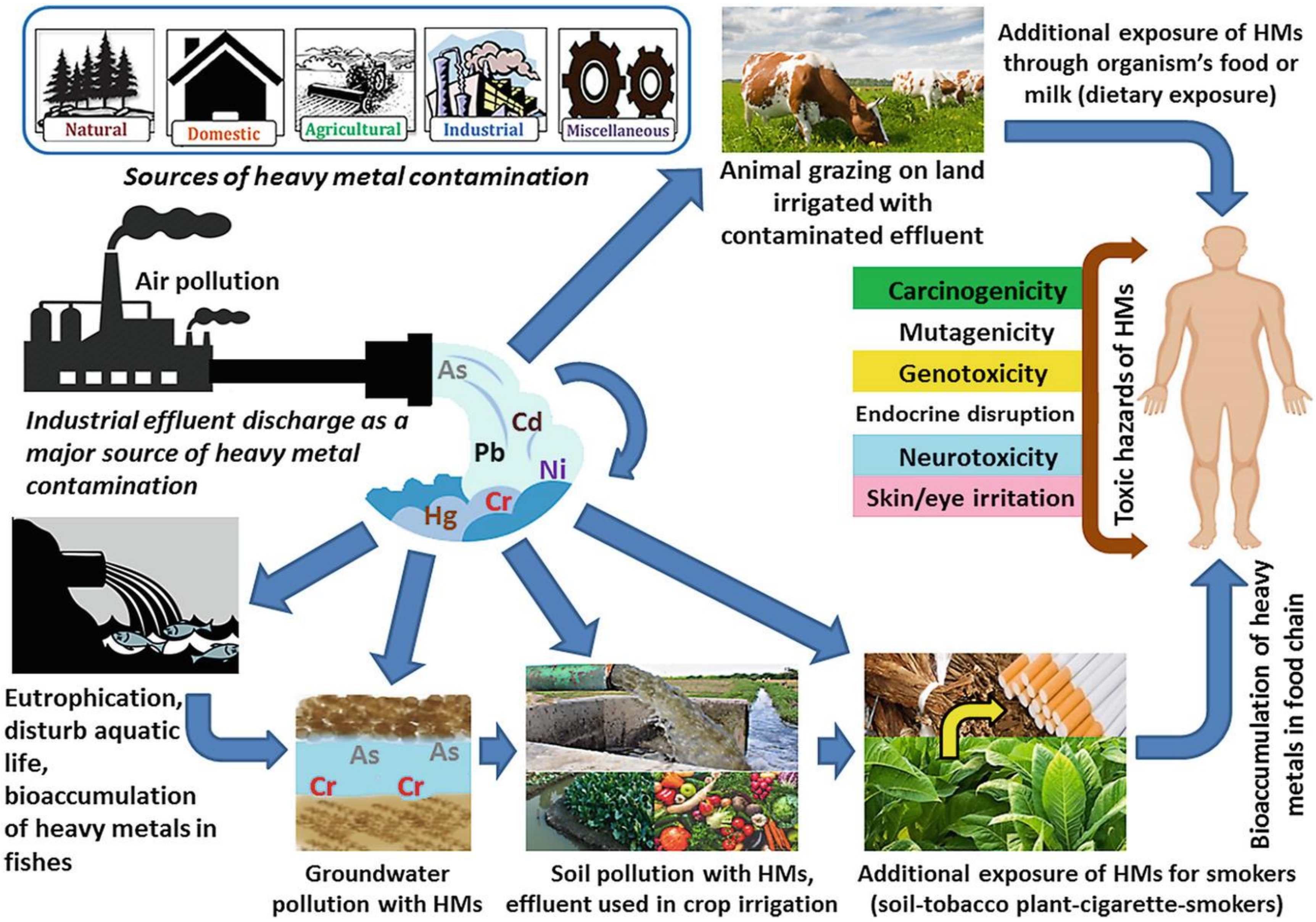
- Globally, C & D waste constitutes ~20 to 30% of total solid waste and ~70 to 80 % of C & D is concrete and masonry
- Fresh cement waste is often dumped into the landfill
  - Occupying space
  - Pollution while transferring and dumping
- Cementitious waste contains C-S-H as one of the main components due to hydration of cement
- C-S-H has been chemically synthesized in many studies and used a novel adsorbent to treat contaminants




**Hardened cement mortar**

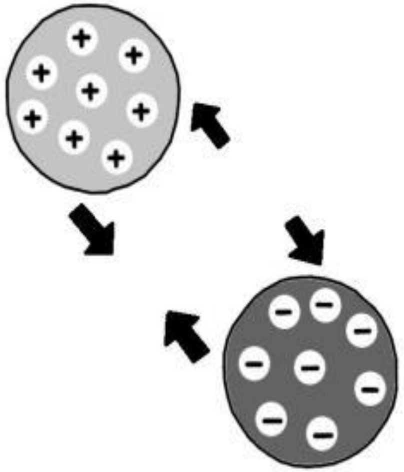
Robayo-Salazar et al. 2020

# Metal pollution in the terrestrial & the aquatic ecosystems

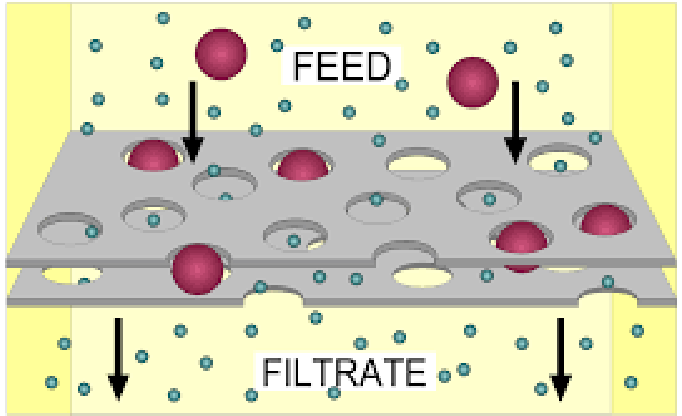



Saxena et al. (2019)

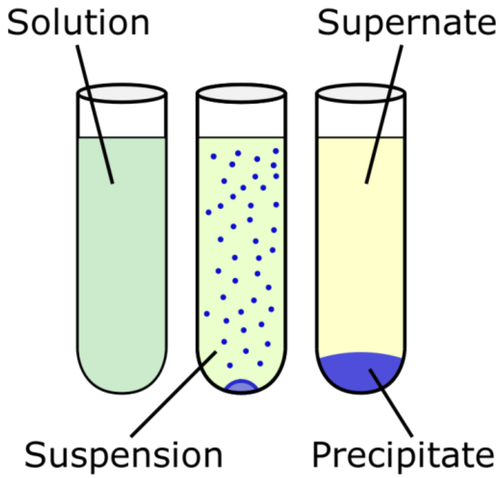
# Conventional removal technologies



Ion Exchange




Filtration




Precipitation

- Limited to specific concentration ranges
- Not economical
- Difficulties in scaling
- Operational issues

Solution

Adsorption

# Adsorption Technology

**Conventional Adsorbents**

- Biochar
- Activated carbon
- Carbon black
- Zeolites
- Resins
- Silica gels

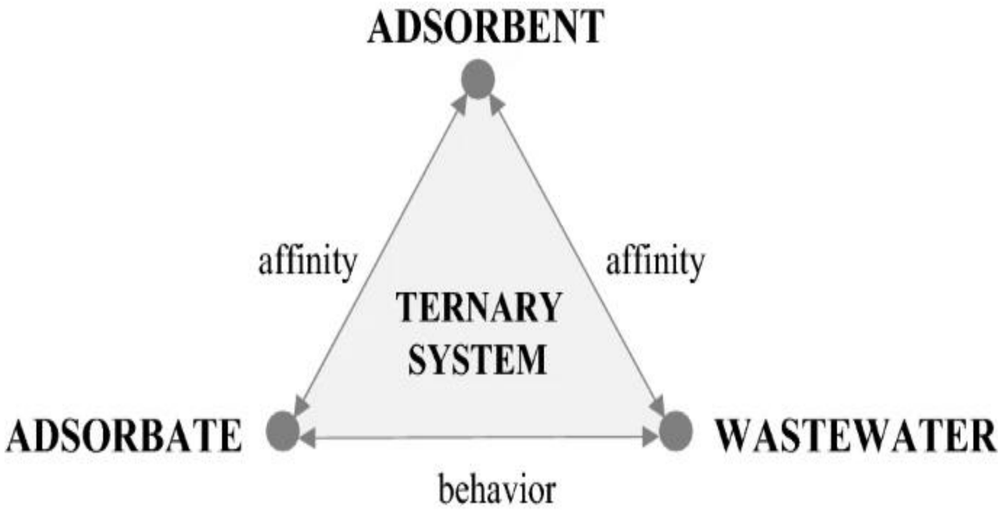
Cons

- Availability in bulk
- Production challenges
- Activation difficulties
- Economy

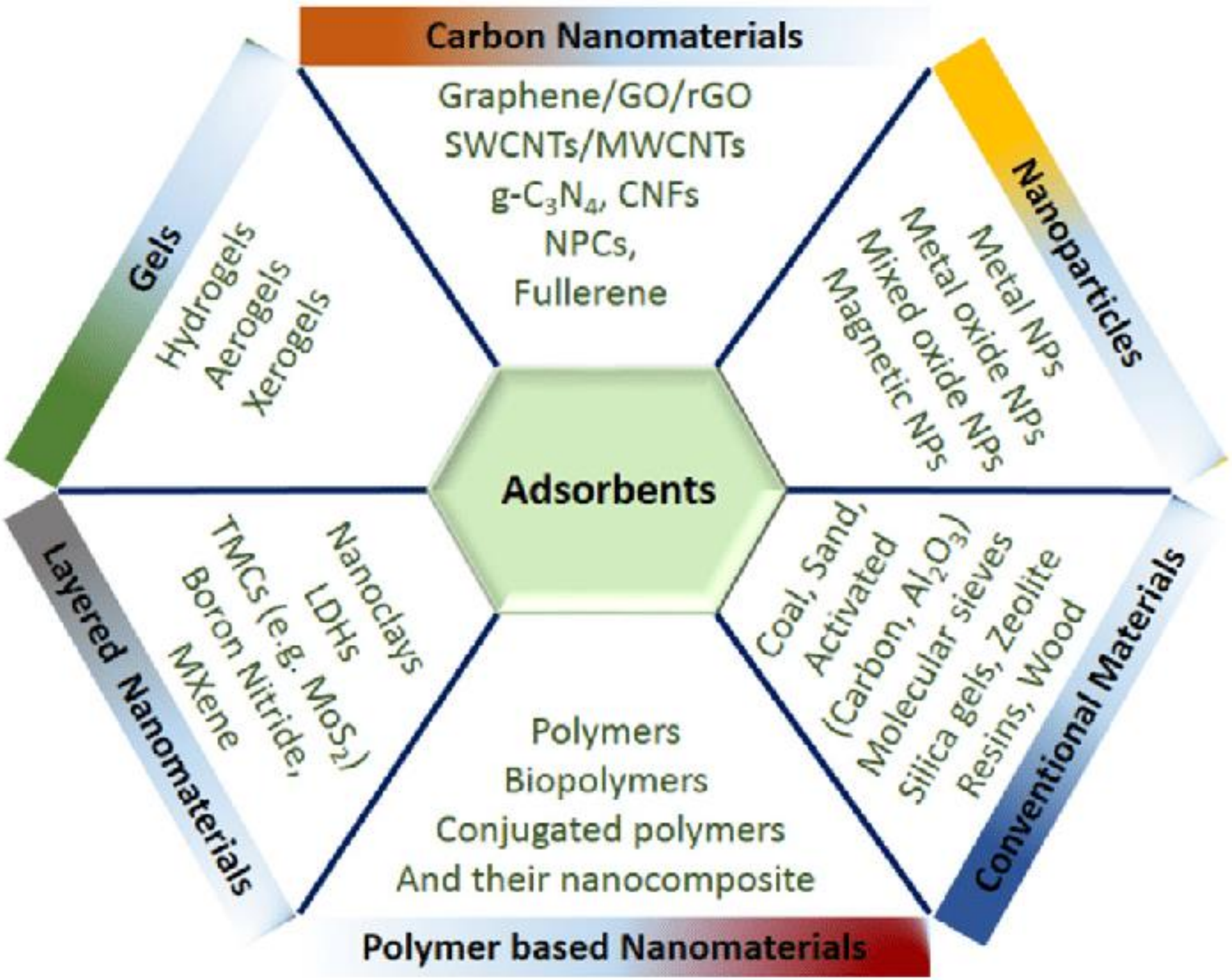
Pros

**Industrial waste**

- Fly ash
- Brick waste
- Clay
- Cementitious waste
- Siliceous waste
- Mud waste



# Adsorbent Types




*Dearth of information on the combined effect of* ***biochar & cementitious material*** *as adsorbent for removal of metals from aqueous solution*

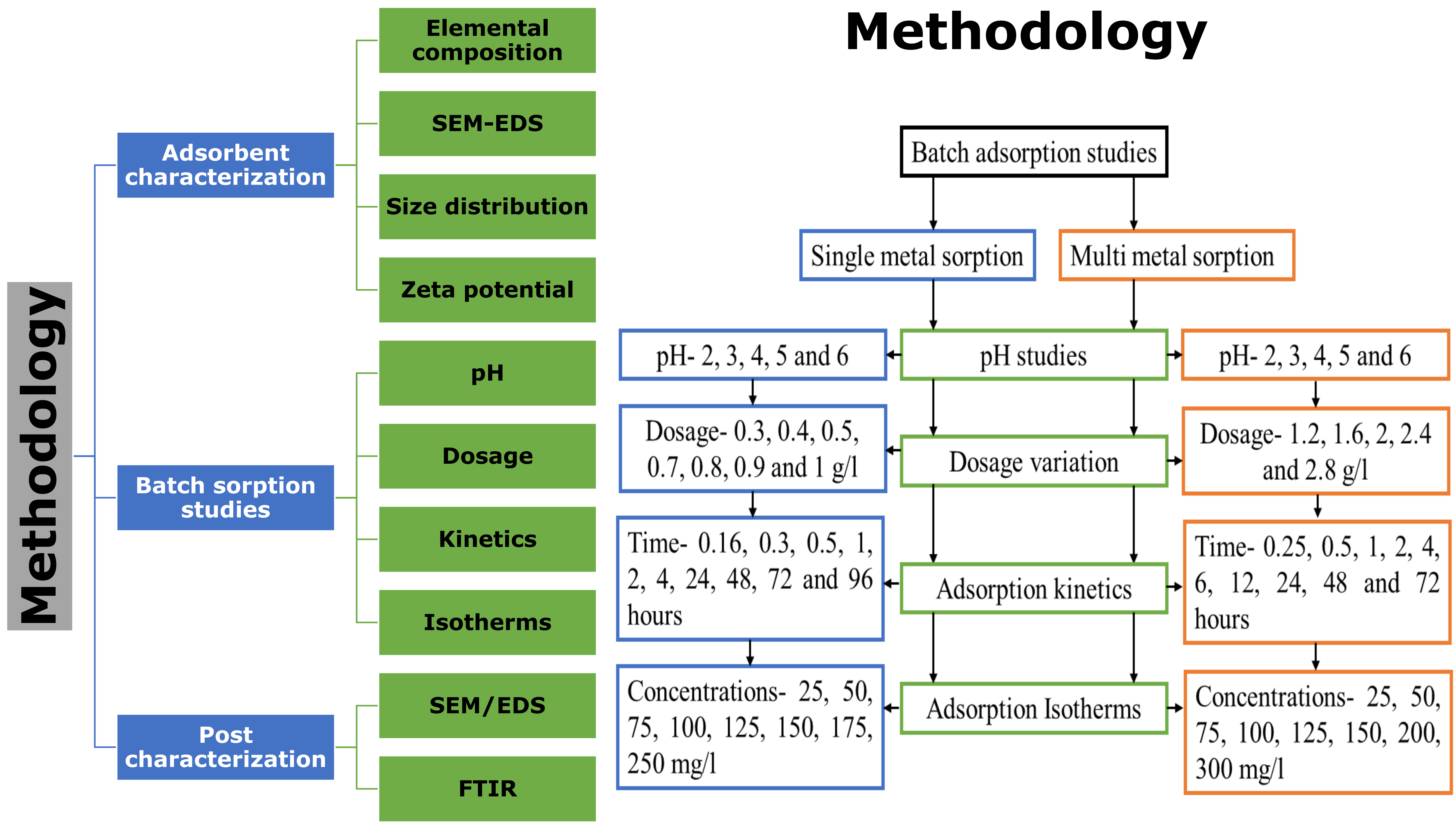
# Overarching aim

***The overarching aim was to determine the removal efficiency of three selected metals ($Pb^{2+}$, $Cu^{2+}$, and $Zn^{2+}$) from water by biochar admixture crushed cement mortars***

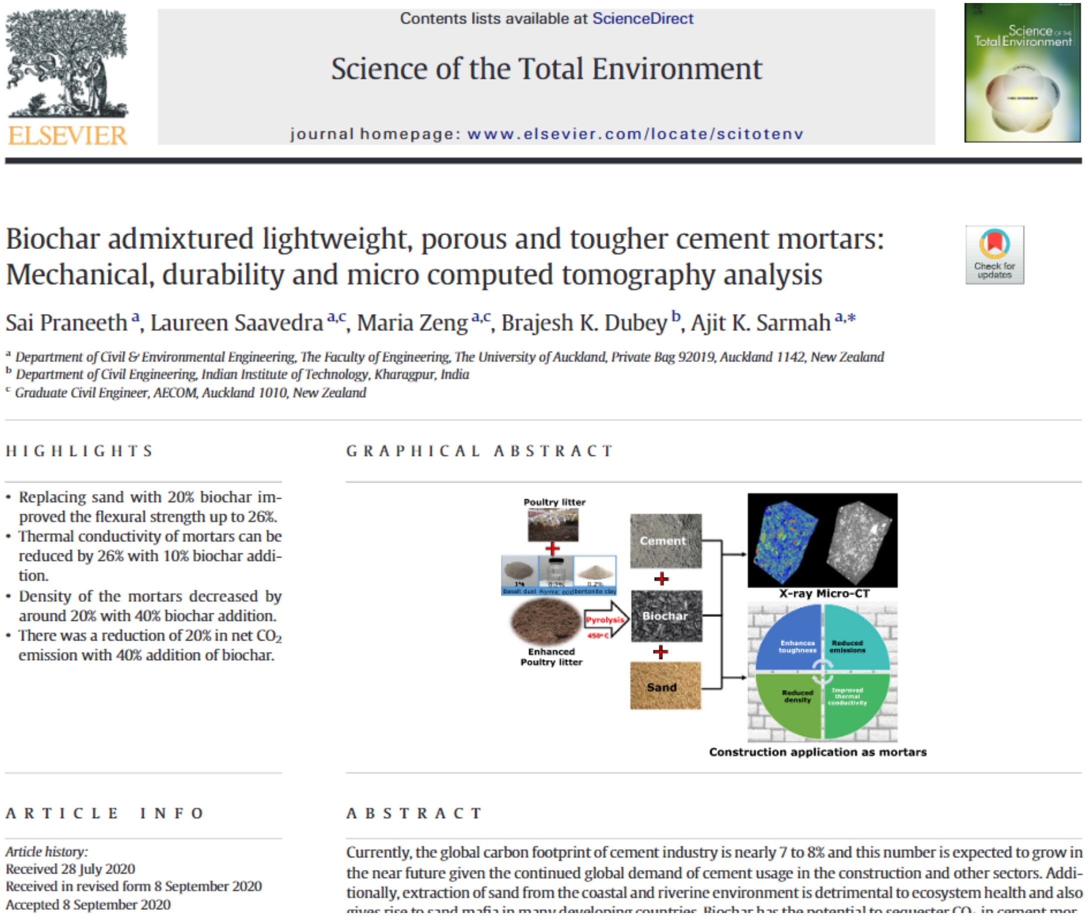
## Specific Objectives

1. **to understand the effect biochar dosage on the adsorbent's capacity to remove metals from aqueous solution**

2. **to compare monometal and multimetal adsorption characteristics and patterns in a batch experiment**


Methodology
Methodology
Adsorbent characterization
Elemental composition
SEM-EDS
Size distribution
Zeta potential
Batch sorption studies
pH
Dosage
Kinetics
Isotherms
Post characterization
SEM/EDS
FTIR
Batch adsorption studies
Single metal sorption
Multi metal sorption
pH studies
pH- 2, 3, 4, 5 and 6
pH- 2, 3, 4, 5 and 6
Dosage variation
Dosage- 0.3, 0.4, 0.5, 0.7, 0.8, 0.9 and 1 g/l
Dosage- 1.2, 1.6, 2, 2.4 and 2.8 g/l
Adsorption kinetics
Time- 0.16, 0.3, 0.5, 1, 2, 4, 24, 48, 72 and 96 hours
Time- 0.25, 0.5, 1, 2, 4, 6, 12, 24, 48 and 72 hours
Adsorption Isotherms
Concentrations- 25, 50, 75, 100, 125, 150, 175, 250 mg/l
Concentrations- 25, 50, 75, 100, 125, 150, 200, 300 mg/l

# Adsorbent preparation



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ELSEVIER

Biochar admixtured lightweight, porous and tougher cement mortars: Mechanical, durability and micro computed tomography analysis

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HIGHLIGHTS

- Replacing sand with 20% biochar improved the flexural strength up to 26%.
- Thermal conductivity of mortars can be reduced by 26% with 10% biochar addition.
- Density of the mortars decreased by around 20% with 40% biochar addition.
- There was a reduction of 20% in net $CO_2$ emission with 40% addition of biochar.

GRAPHICAL ABSTRACT

Poultry litter
Cement
Biochar
Sand
Pyrolysis
Enhanced Poultry litter
X-ray Micro-CT
Construction application as mortars

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ABSTRACT

Currently, the global carbon footprint of cement industry is nearly 7 to 8% and this number is expected to grow in the near future given the continued global demand of cement usage in the construction and other sectors. Additionally, extraction of sand from the coastal and riverine environment is detrimental to ecosystem health and also

Sand

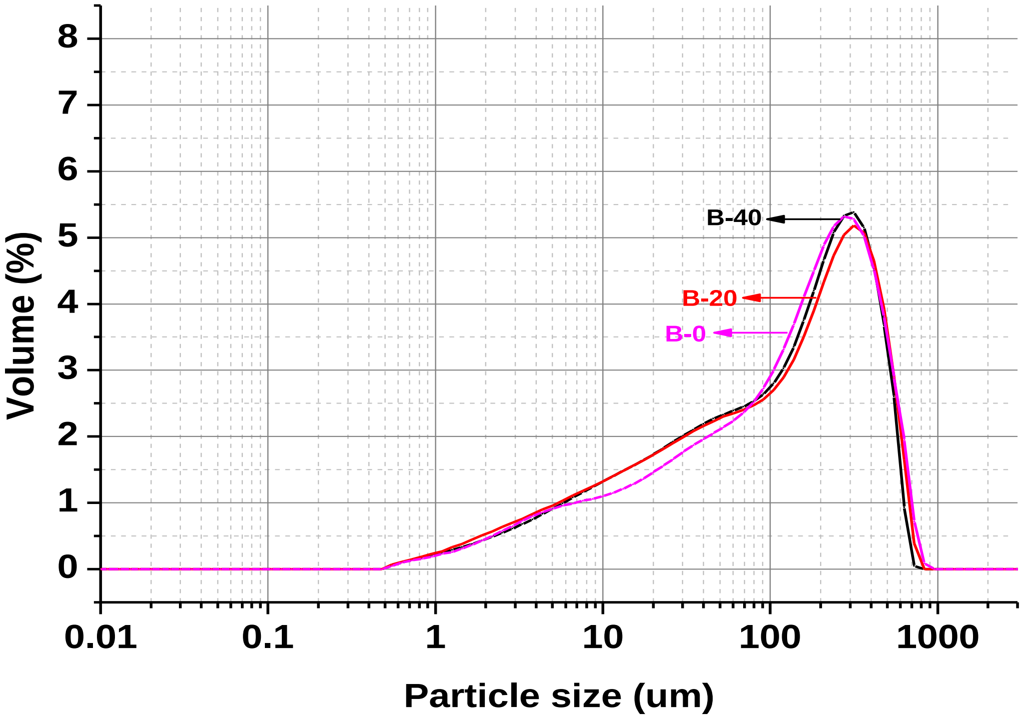
Biochar

Cement

Mortars

↓

Crushed

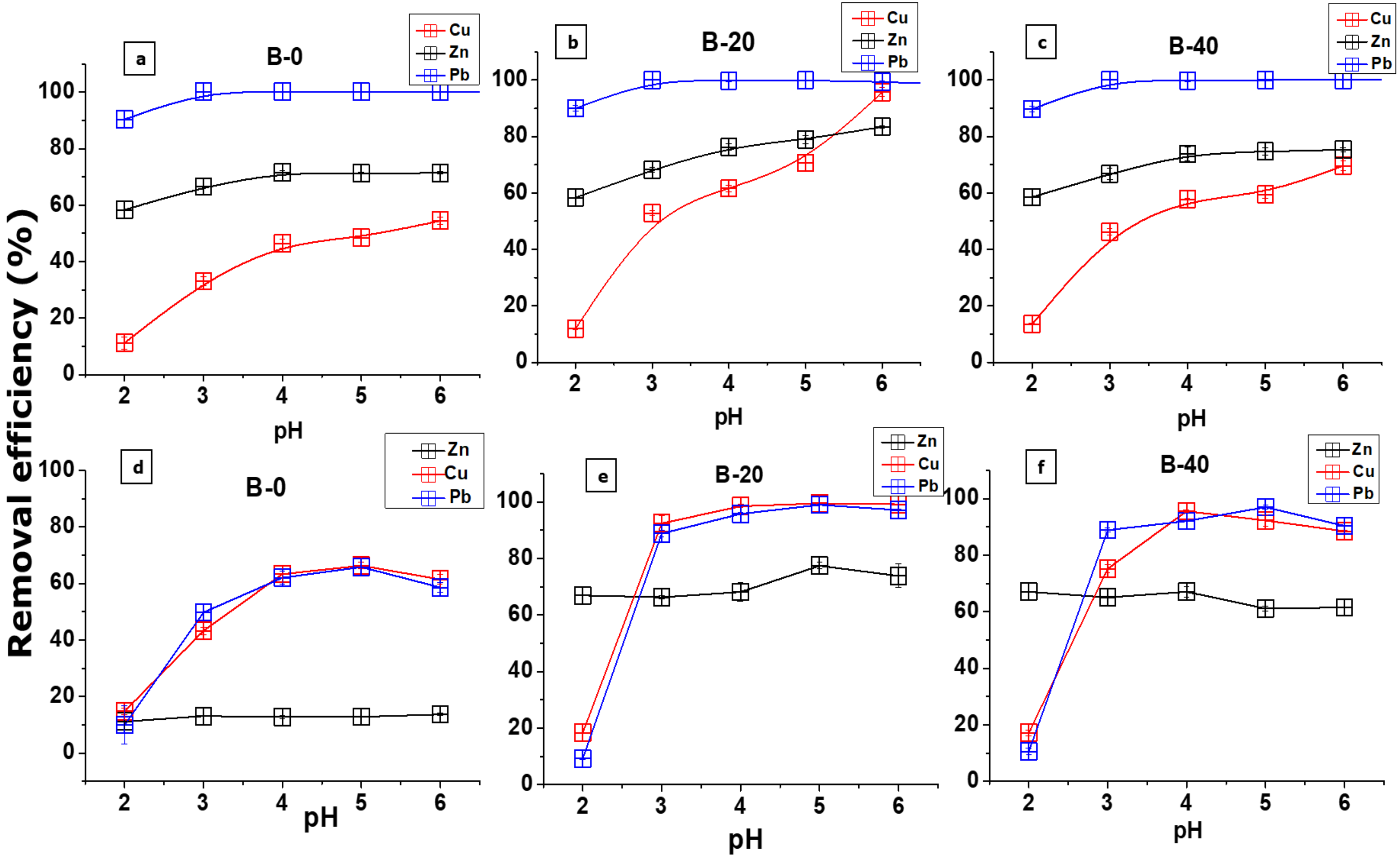


# Composition

| Oxides | Cement (%) | BC-0 (%) | BC-20 (%) | BC-40 (%) |
|---|---|---|---|---|
| $SiO_2$ | 19.9 | 46.1 | 44.75 | 42.54 |
| $Al_2O_3$ | 5.54 | 10.99 | 10.06 | 9.02 |
| $TiO_2$ | 0.26 | 0.31 | 0.38 | 0.42 |
| MnO | 0.09 | 0.06 | 0.07 | 0.08 |
| $Fe_2O_3$ | 3.11 | 2.857 | 3.33 | 3.6 |
| MgO | 1.39 | 1.44 | 1.76 | 2.0 |
| $Na_2O$ | 0.38 | 2.94 | 2.62 | 2.1 |
| $K_2O$ | 0.38 | 0.48 | 0.59 | 0.63 |
| $P_2O_5$ | 0.11 | 0.08 | 0.592 | 1.16 |
| CaO | 64 | 22.73 | 21.33 | 21.43 |

**On hydration, the oxides present in the cement is transformed into calcium silicate hydrate (CSH)**

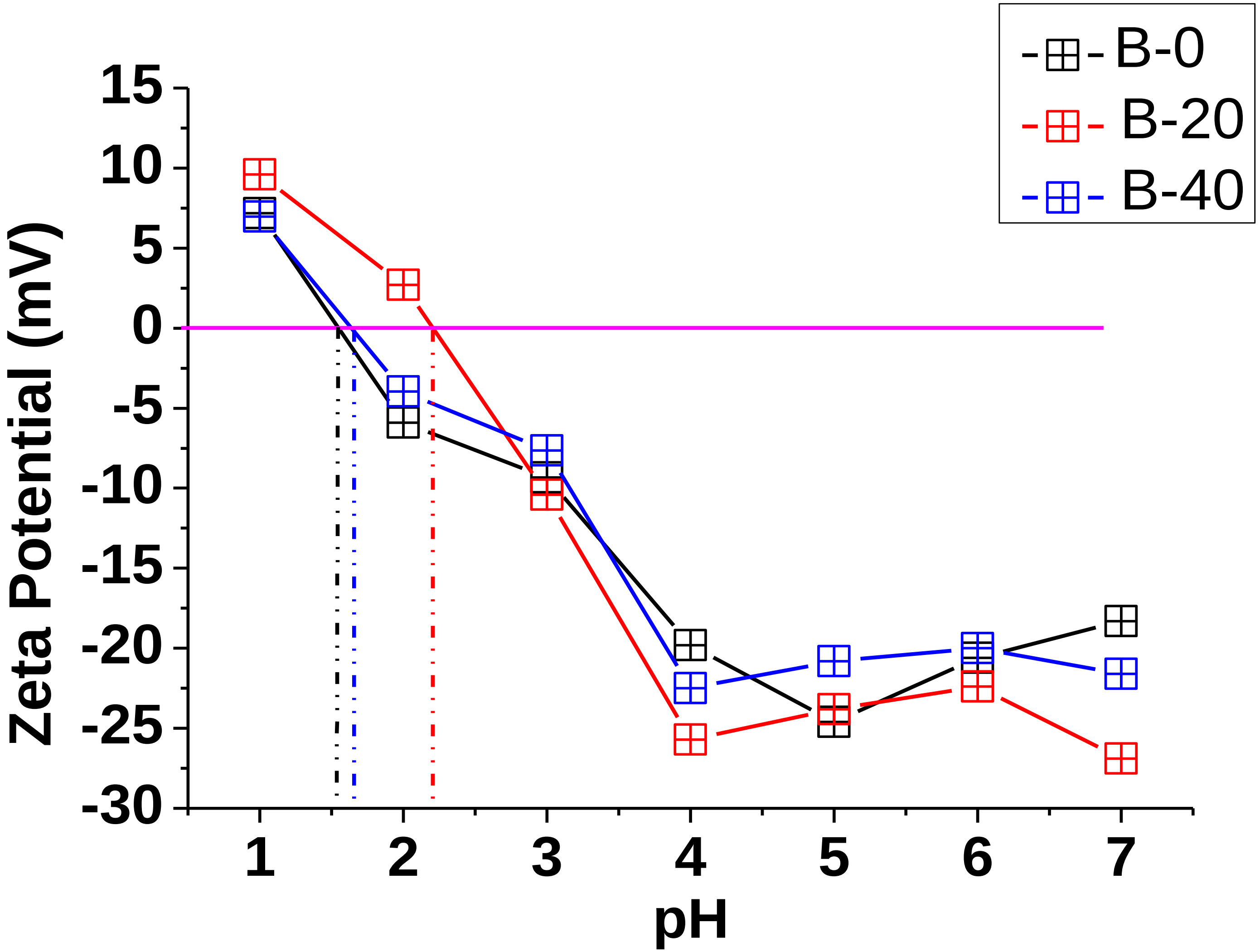
# pH studies



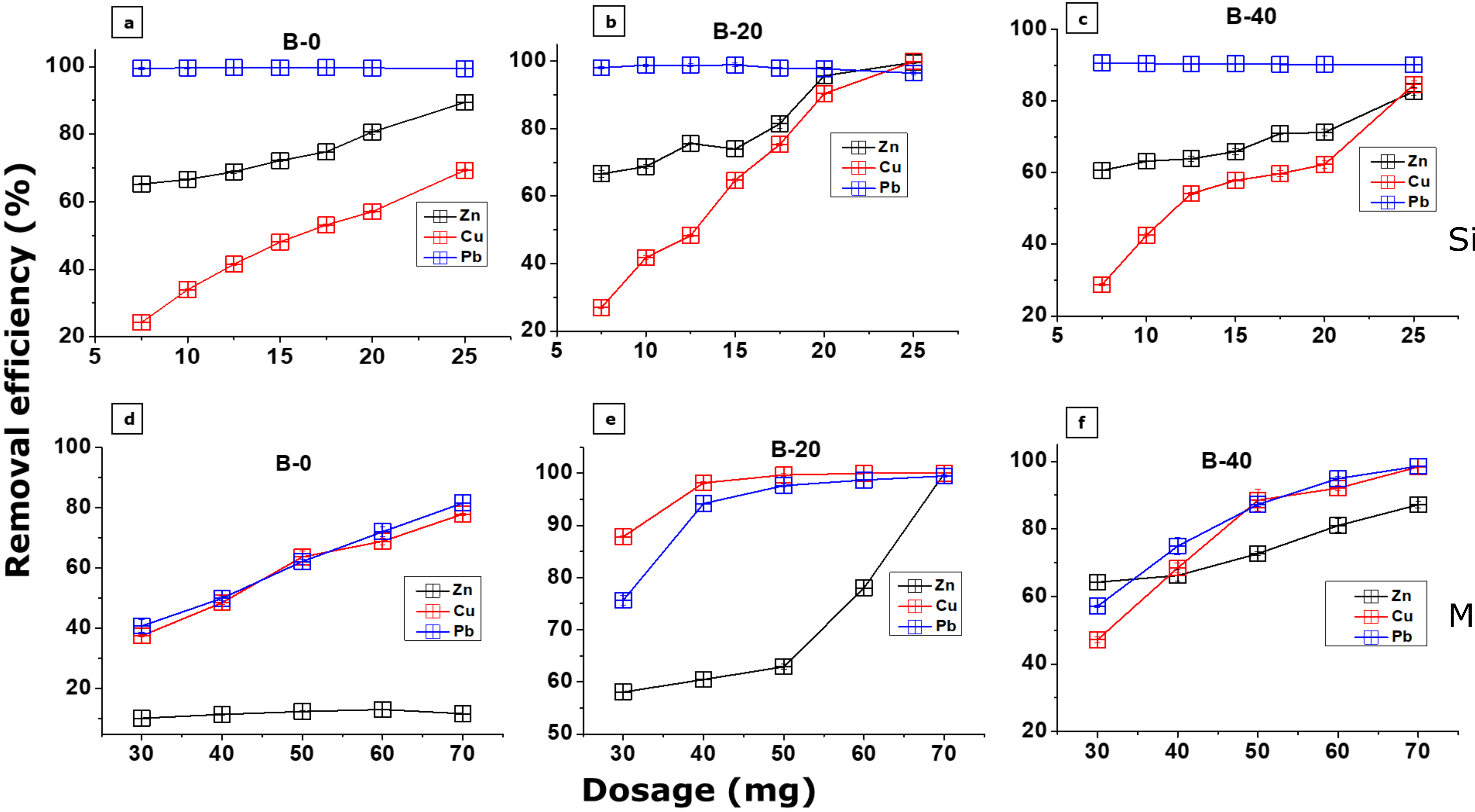

Single metal

Multi metal

# pH studies



# Dosage studies




Single metal

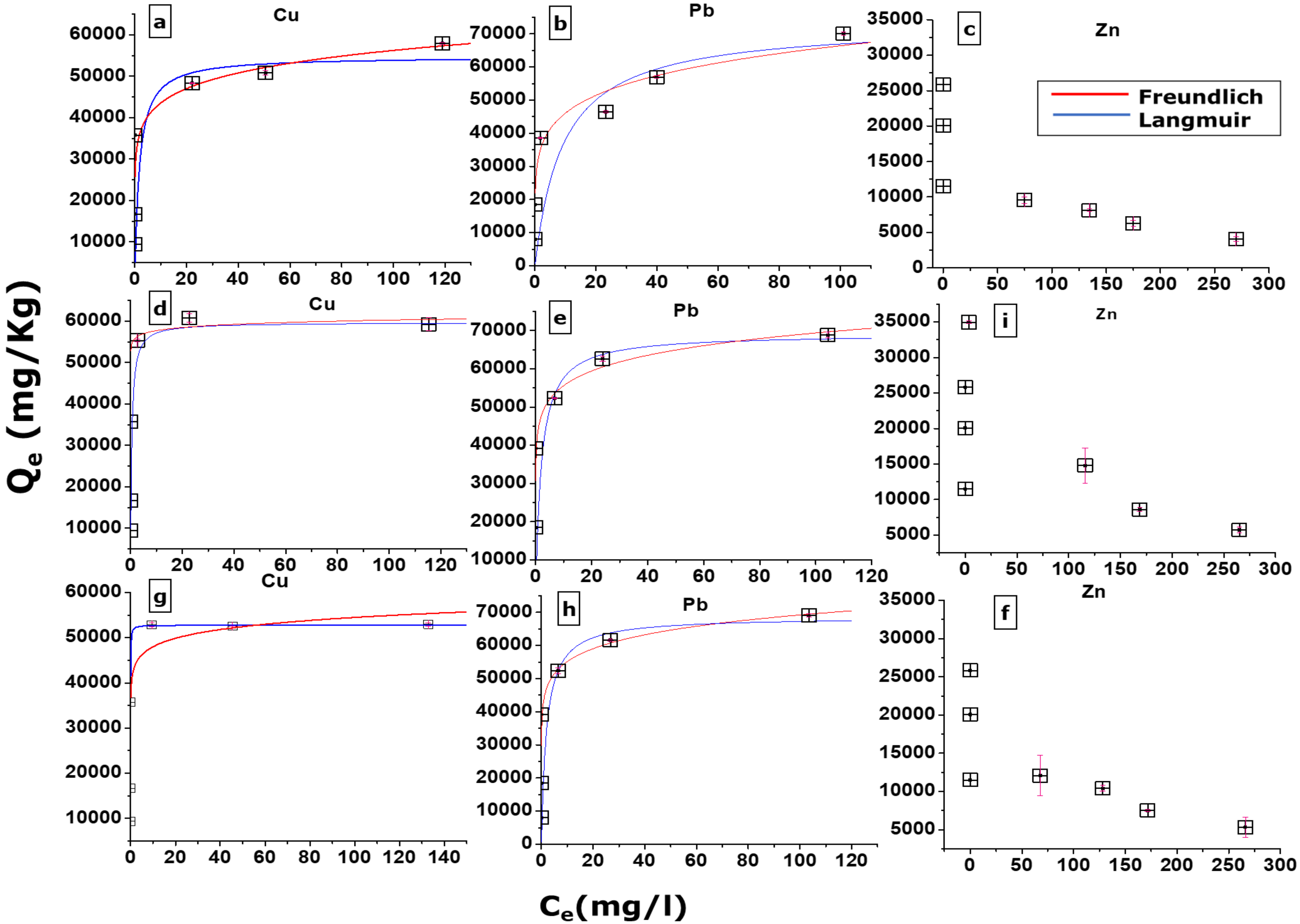
Multi metal

# Single metal Isotherms

| Adsorbent | Langmuir | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cu | | | | Zn | | | | Pb | | | |
| | $q_m$(mg/g) | $K_L$(L/mg) | $R_L$ | $R^2$ | $q_m$(mg/g) | $K_L$(L/mg) | $R_L$ | $R^2$ | $q_m$(mg/g) | $K_L$(L/mg) | $R_L$ | $R^2$ |
| **BC - 0** | 64.103 | 1.835 | 0.003 | 0.999 | 128.205 | 0.464 | 0.009 | 0.994 | 400.000 | 0.926 | 0.0002 | 0.998 |
| **BC - 20** | 103.093 | 0.362 | 0.013 | 0.977 | 112.360 | 7.417 | 0.0006 | 0.999 | 333.333 | 6 | 0.0002 | 0.999 |
| **BC - 40** | 80.645 | 0.7561 | 0.006 | 0.999 | 123.457 | 0.435 | 0.009 | 0.996 | 476.190 | 1.4 | 0.0009 | 0.999 |

| | Freundlich | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Cu | | | Zn | | | Pb | | |
| | $K_f$ ($mg^{1-n}L^n/g$) | N | $R^2$ | $K_f$ ($mg^{1-n}L^n/g$) | N | $R^2$ | $K_f$ ($mg^{1-n}L^n/g$) | N | $R^2$ |
| **BC - 0** | 37.342 | 0.131 | 0.856 | 61.235 | 0.169 | 0.783 | 136.678 | 0.132 | 0.284 |
| **BC - 20** | 60.855 | 0.113 | 0.632 | 77.911 | 0.096 | 0.679 | 154.632 | 0.141 | 0.432 |
| **BC - 40** | 45.331 | 0.123 | 0.344 | 65.293 | 0.137 | 0.743 | 164.930 | 0.209 | 0.509 |

# Multi metal Isotherms

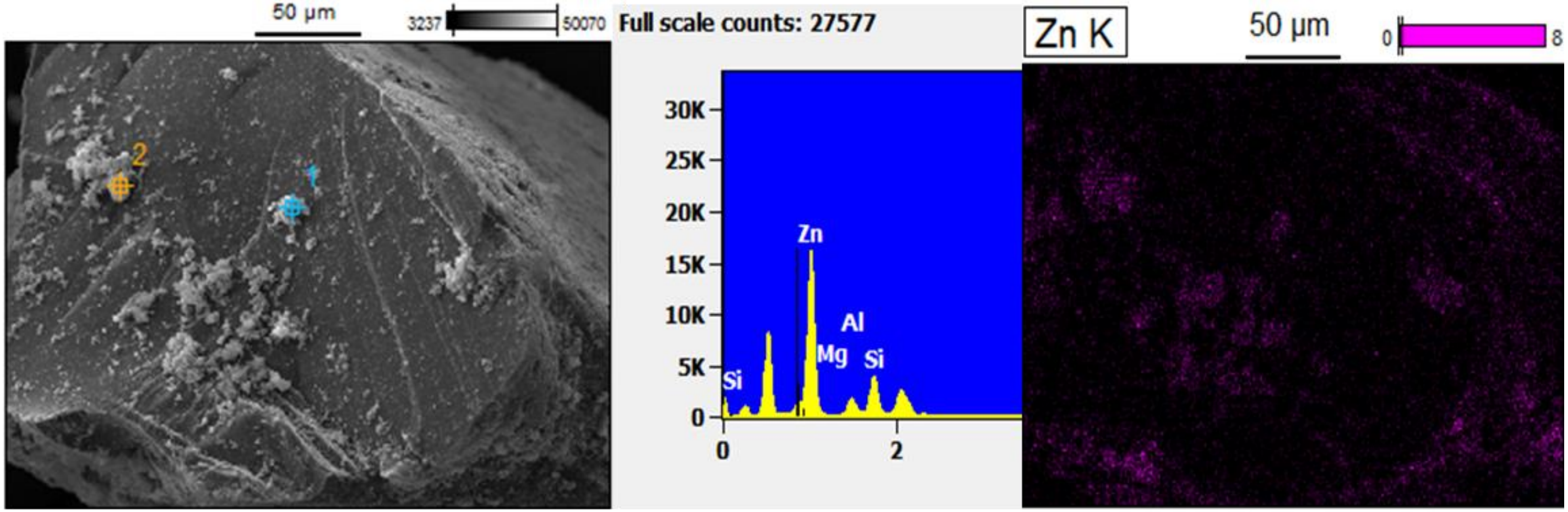


# Multi metal Isotherms

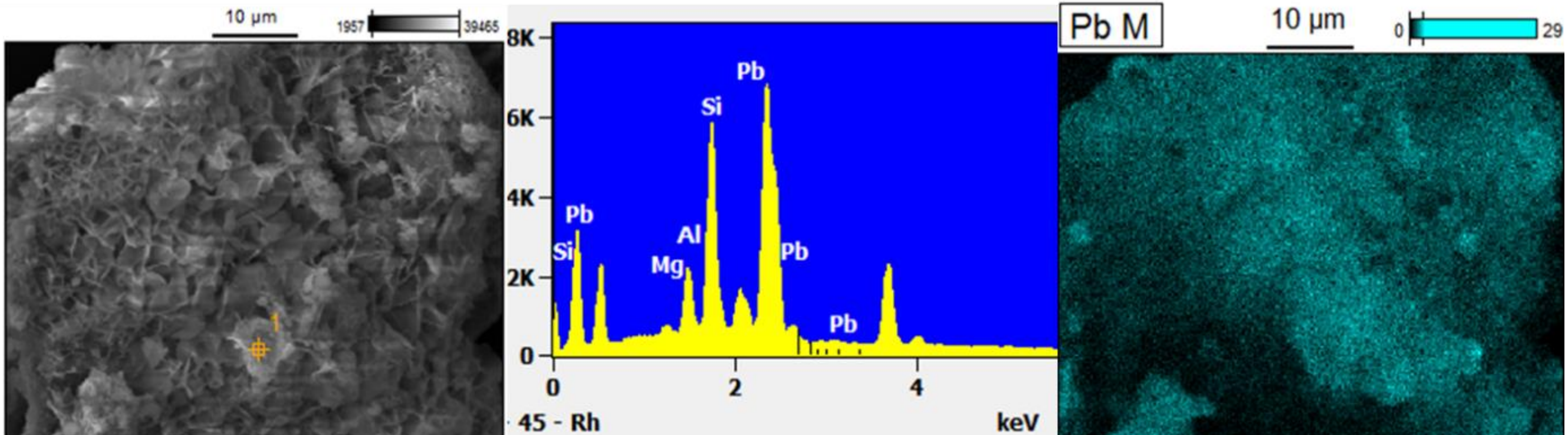
| **Adsorbent** | **Langmuir** | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **Cu** | | | | **Pb** | | | |
| | **$q_m$(mg/g)** | **$K_L$(L/mg)** | **$R_L$** | **$R^2$** | **$q_m$(mg/g)** | **$K_L$(L/mg)** | **$R_L$** | **$R^2$** |
| **BC - 0** | 58.82 | 0.582 | 6.07*10-3 | 0.994 | 70.12 | 0.274 | 12.17*10-3 | 0.977 |
| **BC - 20** | 59.20 | 17.72 | $20.10*10^{-3}$ | 0.999 | 68.49 | 1.21 | $2.7*10^{-3}$ | 0.999 |
| **BC - 40** | 53.19 | 9.35 | $3.8*10^{-4}$ | 0.998 | 73.2 | 0.945 | 3.51*10-3 | 0.998 |

| | **Freundlich** | | | | | |
|---|---|---|---|---|---|---|
| | **Cu** | | | **Pb** | | |
| | **$K_f$ ($mg^{1-n}L^n$/g)** | **N** | **$R^2$** | **$K_f$ ($mg^{1-n}L^n$/g)** | **N** | **$R^2$** |
| **BC - 0** | 33.96 | 0.108 | 0.339 | 34.11 | 0.138 | 0.341 |
| **BC - 20** | 55.08 | 0.02 | 0.55 | 43.95 | 0.1 | 0.44 |
| **BC – 40** | 51.76 | 0.004 | 0.517 | 43.65 | 0.1 | 0.985 |

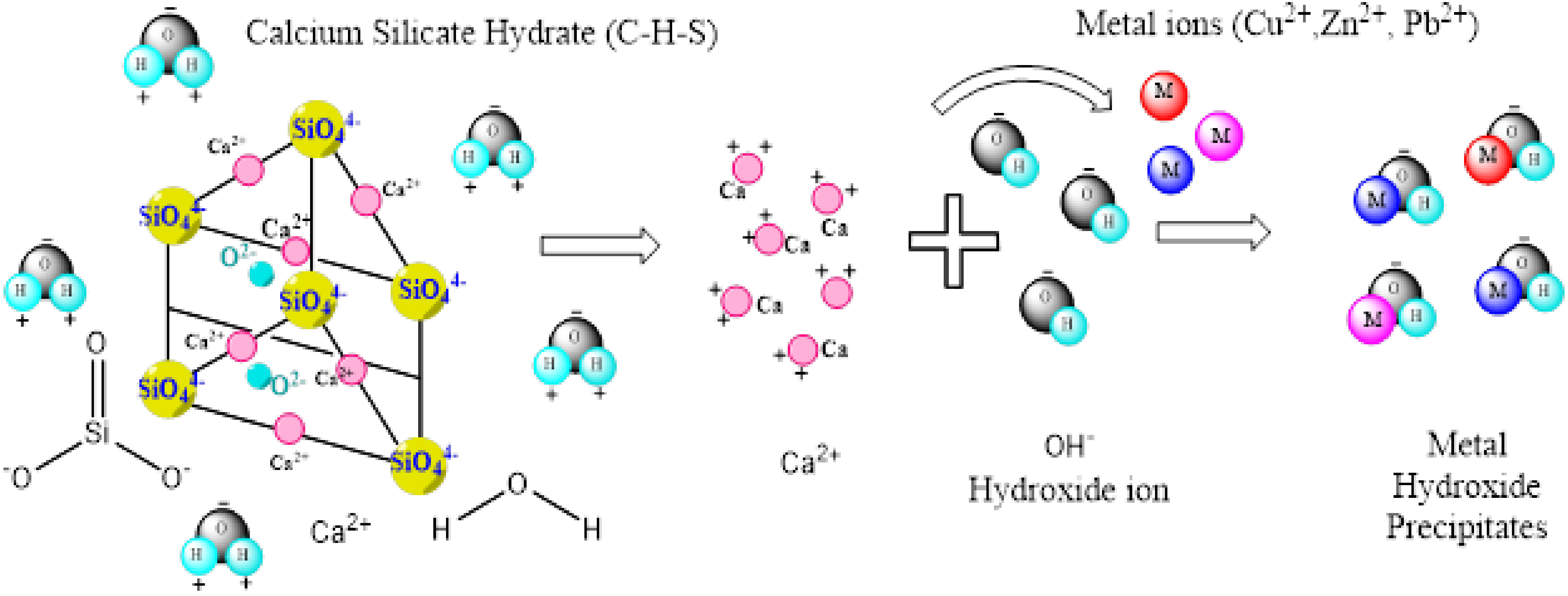
**Adsorbent B-40 after adsorption of Zn at the dosage of 25 mg**




**Mapping of Pb(II) onto B-20 after adsorption for initial concentration of 100 mg/l at pH 5**

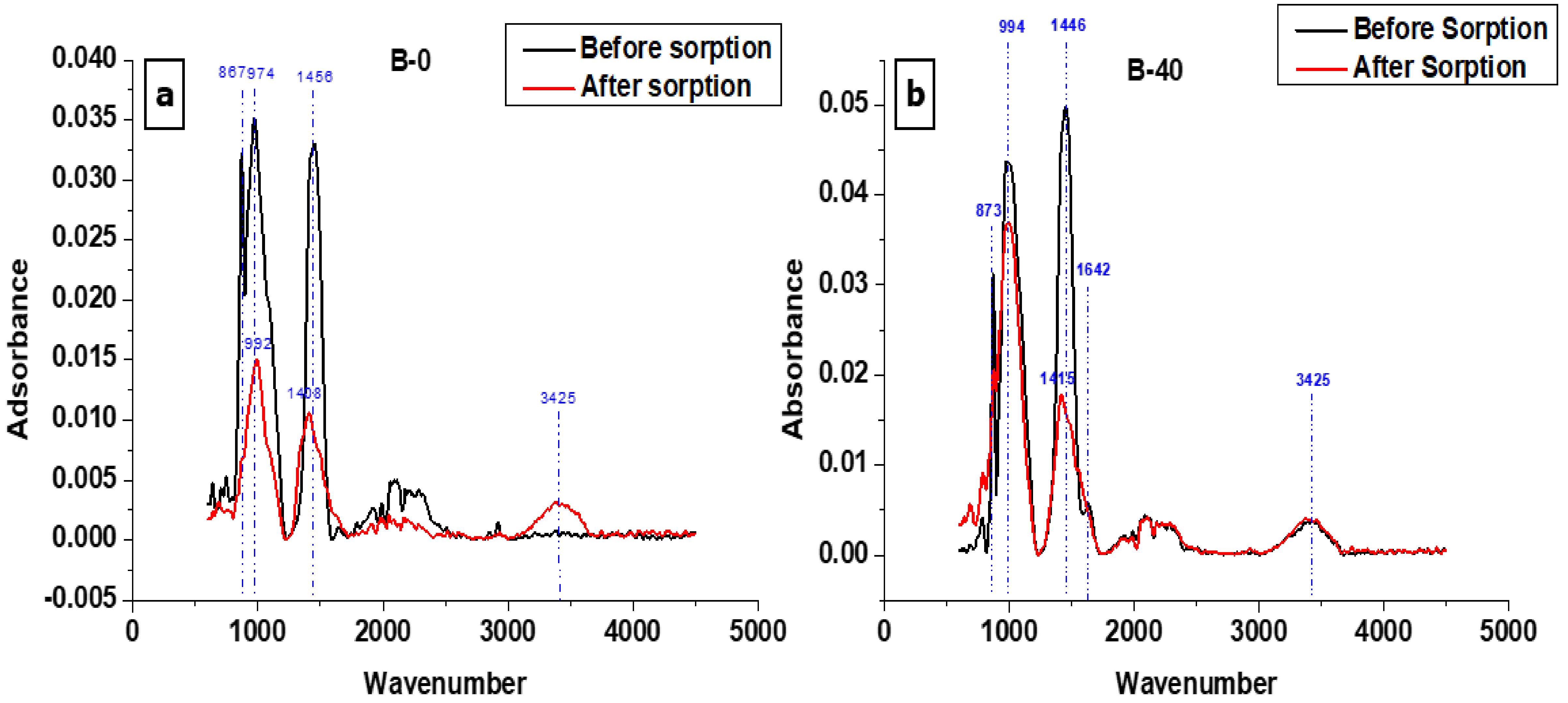


# Plausible Mechanisms




1. **Metal Precipitation**
2. **Metal complexation** → $Pb^{2+}$ and $Zn^{2+}$ forms the insoluble $Ca[Pb(OH)_3]_2$ and $Ca[Zn(OH)_3H_2O]_2$ and $CaZn_2Si_2O_7{\cdot}H_2O$
3. **Ion Exchange** → CSH + $M^{2+}$ $Ca^{2+}$+ $M^{2+}$ $(SH)^-$ (M= $Pb^{2+}$, $Cu^{2+}$ and $Zn^{2+}$)

# Plausible Mechanisms



# Overall optimised parameters

| Adsorbent | Parameter | Single metal adsorption | | | Multimetal adsorption | | |
|---|---|---|---|---|---|---|---|
| | Element | Lead | Copper | Zinc | Lead | Copper | Zinc |
| B-0 | pH | 5 | 5 | 5 | 5 | 5 | 5 |
| | Dosage (mg) | 25 | 25 | 25 | 70 | 70 | 70 |
| | Time (hours) | 24 | 24 | 24 | 48 | 48 | 48 |
| | Adsorption capacity (mg/g) | 400 | 64 | 128 | 70 | 59 | 25 |
| B-20 | pH | 5 | 5 | 5 | 5 | 5 | 5 |
| | Dosage (mg) | 20 | 20 | 20 | 70 | 70 | 70 |
| | Time (hours) | 24 | 24 | 24 | 12 | 12 | 12 |
| | Adsorption capacity (mg/g) | 333 | 103 | 112 | 68 | 59 | 35 |
| B-40 | pH | 5 | 5 | 5 | 5 | 5 | 5 |
| | Dosage (mg) | 25 | 25 | 25 | 70 | 70 | 70 |
| | Time (hours) | 24 | 24 | 24 | 12 | 12 | 12 |
| | Adsorption capacity (mg/g) | 476 | 81 | 123 | 73 | 53 | 26 |

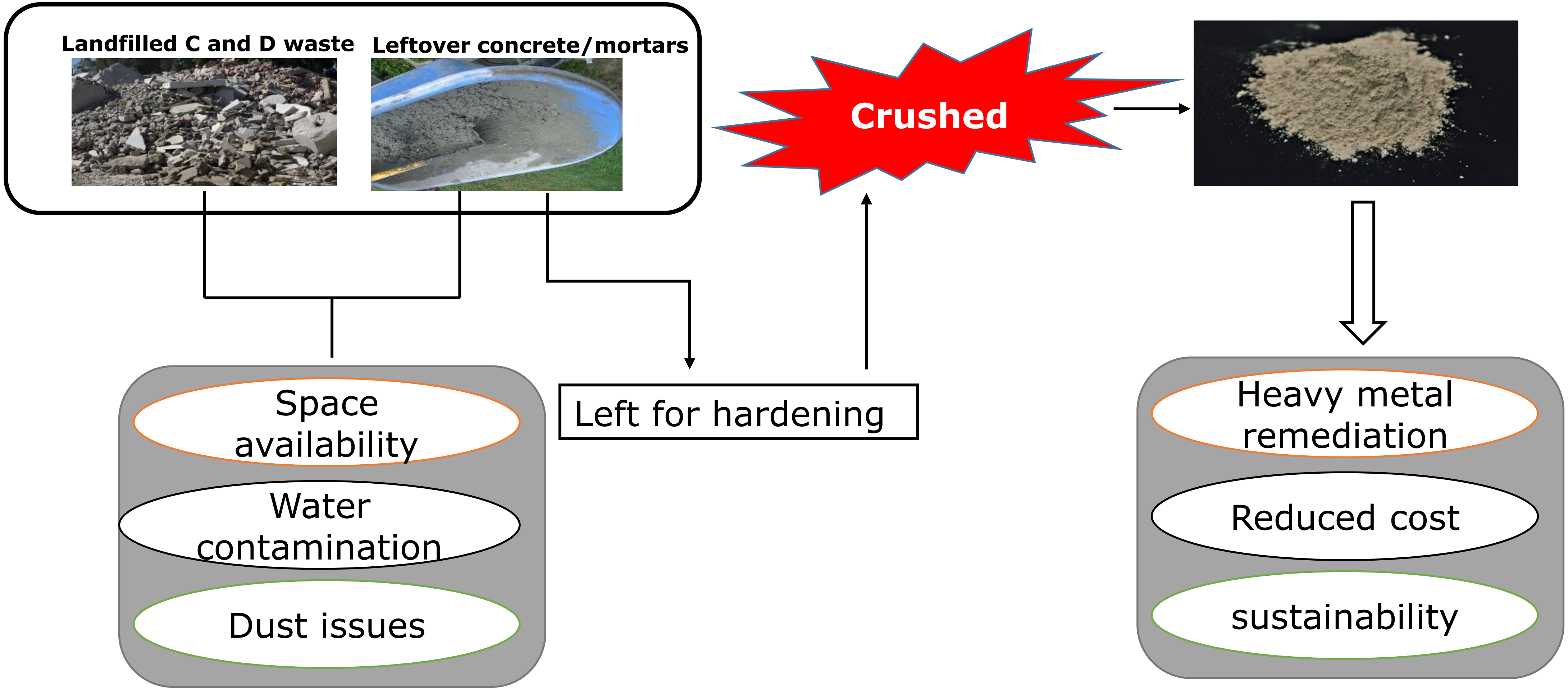
# Literature data on sorption capacity

| Adsorbent | $Pb^{2+}$ (mg/g) | $Cu^{2+}$ (mg/g) | $Zn^{2+}$ (mg/g) | Reference |
|---|---|---|---|---|
| Lime sand brick waste | - | 7 | - | (X. Zhang et al., 2019) |
| Sol-gel derived CSH | 543 | | | (Z. Zhang et al., 2018) |
| Crushed concrete fines | 37 | 35 | 33 | (Coleman et al., 2005) |
| CSH derived from steel slag | 273 | 244 | 508 | (Shao et al., 2018) |
| CSH derived from blast furnace slag | - | 80.4 | - | (Kuwahara et al., 2013) |
| CSH derived from oyster shells | - | 203 | - | (You et al., 2016) |
| Autoclave aerated concrete fines | 250 | - | - | (Kumara et al., 2019) |
| Cement admixtures zeolite | 932 | 154 | | (Lim et al., 2019) |
| Iron- modified CSH | - | 25.83 | - | (Valenzuela et al., 2021) |
| Biochar admixture cement mortars | 476 | 80 | 123 | This study |

# Techno-economic feasibility

*It is estimated that globally around 165-305 million tonnes of fresh concrete end up as waste every day*

The cost of adsorbents used will be minimal as compared to conventional adsorbents such as activated carbon ($5.6/Kg) and biochar ($5 /Kg)



# Salient findings:

- A dosage of 20 mg for single metal and 70 mg for multi-metal of an adsorbent dose was found to be sufficient to remove about 70-90% of the three heavy metals

- The adsorbent capacity for $Pb^{2+}$, $Cu^{2+}$, and $Zn^{2+}$ were 473, 89, and 127 mg/g, which is comparable or higher than conventional activated carbon systems for metal removal.

- The use of hardened cementitious waste for treating metals in aqueous media can avoid issues such as space availability and dust arising from disposal scenario.

- The optimization datasets of different parameters (pH, dosage, associated kinetics) could be useful for comparison purposes for future in designing pilot scale plant.

- Overall, potential exists for mortar fines to be used as an economical and efficient way to remediate metal contaminated water while promoting sustainability. However, a lot to be explored in future work.


THANK YOU