Performance of Reactive Slag Filters for High Concentration Phosphorus Removal from Aqueous Solution

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Backgrounds

Problems caused by phosphorus in water

- Phosphorus in nonpoint pollution source
  - Agriculture, livestock wastewater, storm water runoff, etc.
  - Causeing eutrophication and harmful algal blooming

(Image adapted from Plan Washington.org).
Materials for phosphorus removal

- Natural and industrial by-product materials
  - Zeolite, limestone, dolomite, steel slag, etc.
Phosphorus removal by steel slag

- Steel slag
  - $\text{Ca}^{2+}$ elution in aqueous phase
  - $\text{PO}_4^{3-}$ removal by precipitation with $\text{Ca}^{2+}$
  - pH increase due to dissociation of CaO to $\text{Ca}^{2+}$ and $\text{OH}^-$ in solution

$\text{Ca}^{2+} + \text{PO}_4^{3-} \rightarrow \text{Ca}_3(\text{PO}_4)_2$
Steel slag coated with CNTs

- Carbon nanotubes (CNTs)
  - A cylindrical shell of graphene sheet
  - Great potential to absorb chemical, dioxin, VOCs, heavy metal, etc.

- CNT functionalization
  - Increase water solubility and adsorption capacity
  - Neutralizing reaction by electrostatic attraction between the functionalized group and divalent ions
To evaluate the properties of a reactive CNT–coated steel slag filter to remove phosphorus in aqueous solution

- Studies for CNT functionalization and coating
- Evaluation the adsorption and precipitation capacity
- Optimal conditions for efficient phosphorus removal
Table 1. Chemical composition of the steel slag (Lee and Jang, 2004)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>40.1</td>
</tr>
<tr>
<td>SiO₂</td>
<td>14.4</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>10.8</td>
</tr>
<tr>
<td>MgO</td>
<td>7.2</td>
</tr>
<tr>
<td>MnO</td>
<td>3.1</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2.1</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.8</td>
</tr>
</tbody>
</table>

- **Steel slag**
  - Particle size: 2–6 mm
  - Rich in CaO (40.1%)

- **Slag coating reagent**
  - MWCNT (multi walled CNT)
  - HNO₃/H₂SO₄ (CNT functionalization)
  - SDBS (surfactant)

- **Phosphorus solution**
  - KH₂PO₄ solution
Materials and methods

Preparations of CNT-coated steel slag

- CNT functionalization
  \( \Rightarrow \) HNO_3:H_2SO_4 (9:1, v/v) \( \Rightarrow \) sonication (for 1 h)
- CNT coating ink preparation
  \( \Rightarrow \) 70\% etOH with SDBS (1\%, v/v) \( \Rightarrow \) sonication (3 h)
- CNT loading onto slag
  \( \Rightarrow \) Dipping into CNT ink \( \Rightarrow \) removing \( \Rightarrow \) drying at 150\°C
Materials and methods

Operations and analysis

- Batch operations: Batch-type jar tester

<table>
<thead>
<tr>
<th>Table 2. Conditions for batch operation</th>
<th>Table 3. Parameters for PO$_4$-P removal</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Value</strong></td>
<td><strong>Parameters</strong></td>
</tr>
<tr>
<td>Working vol.</td>
<td>pH</td>
</tr>
<tr>
<td>300 mL</td>
<td>PO$_4$–P conc. (mg/L)</td>
</tr>
<tr>
<td>Temperature</td>
<td></td>
</tr>
<tr>
<td>25°C</td>
<td>Amt. of slag (g)</td>
</tr>
<tr>
<td>Agitation speed</td>
<td></td>
</tr>
<tr>
<td>120 rpm</td>
<td></td>
</tr>
<tr>
<td>Period</td>
<td></td>
</tr>
<tr>
<td>4 d</td>
<td></td>
</tr>
</tbody>
</table>

- Analysis
  - CNT coating status: SEM analysis
  - PO$_4$–P: molybdo–vanadate spectrophotometric method
  - pH: pH meter
Results and discussion

Ca$^{2+}$ elution of steel slag

- Ca$^{2+}$ elution
  - pH increase indicated the CaO dissociation to Ca$^{2+}$ and OH$^-$
  - pH increased dramatically to 11.3 and maintained for 24 h
  - pH decrease due to the dissolution of atmospheric CO$_2$

Fig. 1. pH variations of distilled water by steel slag according to the elution time.
pH variation in D.W. and PO$_4$-P solution

- pH increase
  ⇒ Due to the OH$^-$ release
- Lowering pH
  ⇒ Hydroxyapatite generated by the consumption of OH$^-$ in the P-containing solution

Fig. 2. Comparison of the pH change between distilled water and K$_2$HPO$_4$ solution with steel slag according to the elution time.
Fig. 3. SEM images of the uncoated (A) and CNT-coated (B) steel slag.

- CNT coated on the surface of steel slag like a net
Results and discussion

Phosphorus removal characteristics

- Initial PO$_4$–P conc. and pH
  ⇒ 250 mg/L and 6.8

- PO$_4$–P removal efficiency
  ⇒ 50% PO$_4$–P removal within 9 h (uncoated steel slag)
  ⇒ 90% PO$_4$–P removal within 9 h (CNT–coated steel slag)

- pH
  ⇒ CNT coated < uncoated

Fig. 4. Changes in the PO$_4$–P concentration and pH in the K$_2$HPO$_4$ solution with CNT-coated slag and uncoated slag.
Results and discussion

Phosphorus removal characteristics

Fig. 5. Kinetics of the PO₄-P concentration at different amount of CNT-coated steel slag (C₀= 250 mg PO₄-P/L).

Table 4. PO₄-P removal efficiency according to input CNT-coated steel slag for 12 and 24 h

<table>
<thead>
<tr>
<th>CNT-coated steel slag (g)</th>
<th>Final pH</th>
<th>PO₄-P removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>12 h</td>
<td>24 h</td>
</tr>
<tr>
<td>25</td>
<td>9.0</td>
<td>37.1</td>
</tr>
<tr>
<td>50</td>
<td>8.8</td>
<td>50.3</td>
</tr>
<tr>
<td>100</td>
<td>9.4</td>
<td>80.1</td>
</tr>
<tr>
<td>150</td>
<td>9.5</td>
<td>98.2</td>
</tr>
</tbody>
</table>
Results and discussion

Phosphorus removal characteristics

- PO₄⁻P removal
  ⇒ Depends on the initial PO₄⁻P conc.

- pH increase
  ⇒ Not more than 9.5 after all rxn complete
  ⇒ pH neutralization by exchanging between divalent cation (Ca²⁺) and proton in the carboxylic group of CNT

Fig. 6. Kinetics of the PO₄⁻P concentration and changes in pH at various initial PO₄⁻P concentration (CNT-coated steel slag input = 50 g).
Results and discussion

Adsorption isotherm

- Freundlich isotherm equation
  \[ \frac{x}{m} = X = K C_e^{1/n} \]

Fig. 7. Relationship between \( \ln X \) and \( \ln C_e \) based on the Freundlich isotherm equation for CNT-coated steel slag at 25°C.

- Langmuir isotherm equation
  \[ \frac{x}{m} = X = a b C_e (1 + b C_e) \]

Fig. 8. Relationship between \( \frac{1}{X} \) and \( \frac{1}{C_e} \) based on the Langmuir isotherm equation for CNT-coated steel slag at 25°C.
Results and discussion

Adsorption isotherm

Table 5. Freundlich and Langmuir isotherm constant of CNT-coated steel slag

<table>
<thead>
<tr>
<th>Freundlich isotherm constant</th>
<th>Langmuir isotherm constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>K (mg/g) 421.6</td>
<td>a (mg/g) 1250</td>
</tr>
<tr>
<td>1/n 0.33</td>
<td>b (mg/g) 0.47</td>
</tr>
<tr>
<td>R² 0.97</td>
<td>R² 0.84</td>
</tr>
</tbody>
</table>

- 1/n and K value in Freundlich model
  - 1/n: adsorption efficiency
  - K: adsorption capacity

Table 6. Comparison of K value between CNT-coated steel slag and other materials

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>K (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shale</td>
<td>69.2</td>
<td>Tang et al., 2009</td>
</tr>
<tr>
<td>Ironstone</td>
<td>29.7</td>
<td>Tang et al., 2009</td>
</tr>
<tr>
<td>EAF-slag</td>
<td>29.3</td>
<td>Kim et al., 2010</td>
</tr>
<tr>
<td>CNT-coated steel slag</td>
<td>421.6</td>
<td>This study</td>
</tr>
</tbody>
</table>
Conclusions

- Steel slag is a by-product of steel processing and contains CaO, which remove phosphorus by reacting with $\text{PO}_4^-\text{P}$.  

- When slag component dissolves in water, it causes an increase in pH.  

- Acid-functionalized CNTs made the pH decrease in water by exchanging between proton and divalent cation.  

- The CNT-coated steel slag has a great potential to remove P because of its excellent adsorption capacity revealed by Freundlich adsorption isotherm.  

- The CNT-coated steel slag can be a good candidate for phosphorus removal in a wastewater treatment system.
Acknowledgement

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THANK YOU