Novel polymer-based nanocomposites for application in heavy metal pollution remediation

Emerging Researcher Symposium

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10 October 2012
Introduction: SA’s water problem

- SA is a water scarce country

SA Water Resources and Development: Impacts and Opportunities
Introduction: Heavy metals

- Cr, Ni, Cu, Pb, As etc.
- Exposure can cause liver and kidney damage and also cancer
- Heavy metals can accumulate in food sources through heavy metal contamination of soil and plants
Removal of heavy metals

- Small volume applications: ion exchange

- Larger volumes eg. acid mine drainage: neutralisation and precipitation as well as reverse osmosis (membrane process)

- Ion exchange and reverse osmosis although very efficient is expensive (resins and membranes)

- Neutralisation and precipitation is not 100% effective at removing heavy metals at low concentrations <10ppm
Adsorption for removal of heavy metals

- Most well known – activated charcoal/carbon
- Adsorption of atoms, ions or molecules from a gas, liquid, or dissolved solid to a surface – surface phenomenon
- Absorption is a condition in which something takes in another substance - bulk phenomenon
Why use polymers nanocomposites as adsorbents?

• Nanocomposites are composites of polymers and inorganic/organic material where at least one of the components are smaller than 100nm.

• Relative affordability of polymer nanocomposites.

• Relative ease of manufacture of polymer nanocomposites.
Larger surface ~ Increased adsorption
Materials and methods

• Polypyrrole
• Alumina <50nm

• Reagents are combined and polymerized with FeCl$_3$ to form the PPy/Alumina nanocomposite
Analysis of adsorption efficiency

- Adsorption of Cr(VI)

- Adsorption is evaluated at different nanocomposite loadings, different pH’s as well as initial heavy metal concentrations

- Additional studies include studies at 25, 35, and 45°C to determine thermodynamic parameters of adsorption

Potable water < 0.05 ppm Cr(VI)
Surface discharge < 0.1 ppm Cr(VI)

US EPA
Characterisation: Transmission Electron Microscopy

- Alumina
- PPv
ATR-FTIR spectra of a) PPy/Alumina nanocomposite with b) Cr(VI) adsorbed
Characterisation: X-Ray Photoelectron Spectroscopy

(a) PPy/Alumina nanocomposites before Cr(VI) adsorption
(b) PPy/Alumina nanocomposites after Cr(VI) adsorption

Energy/ (KeV)
Process of Cr(VI) adsorption

1. Cr(VI) containing water
2. Nanocomposite
3. Shake at 200rpm for 24hrs at 25°C
4. Filter to separate material from water
5. Analyse for Cr(VI) concentration using UV spectrophotometry
Results – Nanocomposite loading study

pH = 2; Temp = 25°C
Initial concentration = 250mg/L

% Cr(VI) removal vs Alumina/PPy dose / g
Results – pH studies

Initial concentration: 250mg/L; Temperature: 25°C
Results – Kinetics studies

<table>
<thead>
<tr>
<th>$C_0$ [mg/g]</th>
<th>Pseudo-first-order model</th>
<th>Pseudo-second-order model</th>
<th>Intraparticle diffusion model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ [1/min]</td>
<td>$q_e$ [mg/g]</td>
<td>$R^2$</td>
</tr>
<tr>
<td>100</td>
<td>0.092</td>
<td>18.15</td>
<td>0.849</td>
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<tr>
<td>150</td>
<td>0.057</td>
<td>37.59</td>
<td>0.972</td>
</tr>
<tr>
<td>200</td>
<td>0.032</td>
<td>56.89</td>
<td>0.916</td>
</tr>
</tbody>
</table>

Time/s
Results – Adsorption isotherms

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Q_m [mg/g]</th>
<th>b [L/m]</th>
<th>R_L</th>
<th>R^2</th>
<th>K_F [mg/g]</th>
<th>1/n</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>189.59</td>
<td>0.995</td>
<td>0.0022</td>
<td>0.9993</td>
<td>167.89</td>
<td>0.019</td>
<td>0.6863</td>
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<tr>
<td>35</td>
<td>237.03</td>
<td>1.004</td>
<td>0.0021</td>
<td>0.9996</td>
<td>210.31</td>
<td>0.022</td>
<td>0.6591</td>
</tr>
<tr>
<td>45</td>
<td>271.79</td>
<td>1.022</td>
<td>0.0021</td>
<td>0.9997</td>
<td>220.63</td>
<td>0.042</td>
<td>0.9285</td>
</tr>
</tbody>
</table>

pH=2, Dose=2g/L

35°C

45°C
Results – Regeneration experiments

At low Cr(VI) concentrations

At higher Cr(VI) concentrations

% Adsorbed

- Adsorption 1
- Adsorption 2
Results – Co-existing ions

The graph shows the uptake of Cr(VI) in mg/g for different ions: Ni²⁺, Co²⁺, Cu²⁺, NO₃⁻, Zn²⁺, and Cl⁻. The bars represent the uptake at two concentrations: 250 ppm (blue) and 50 ppm (red).
## Summary

<table>
<thead>
<tr>
<th>Material Characteristic</th>
<th>PPy/Alumina</th>
<th>PPy/Magnetite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max adsorption capacity (25°C)</td>
<td>~190mg Cr(VI)/g material</td>
<td>~169 Cr(VI)/g material</td>
</tr>
<tr>
<td>Time for 100% removal (100ppm, 150ppm, 200ppm)</td>
<td>20min, 80min, 100min</td>
<td>20min, 110min, 150min</td>
</tr>
<tr>
<td>Kinetic model</td>
<td>Pseudo-second order</td>
<td>Pseudo-second order</td>
</tr>
<tr>
<td>Isotherm model</td>
<td>Langmuir</td>
<td>Langmuir</td>
</tr>
</tbody>
</table>

Cr(VI) free water

Magnetic stirrer

Conclusions

• Developed a PPy/Alumina nanocomposite

• Improved adsorption capacity for Cr(VI) when compared to Fe₃O₄ nanocomposite and other low cost materials

• Regeneration up to 3 cycles was possible at low Cr(VI) concentrations

• Co-existing ion studies showed material specificity for Cr(VI)
Acknowledgements

• Dr Arjun Maity, Supervisor
• Dr James Wesley-Smith, Nanocenter, TEM images
• Mrs Avashnee Chetty, Group leader
Thank you

Questions?