Removal of Chromium(VI) from aqueous solution using ZnO nanoparticles an investigation in to the effects light and dark conditions on the binding.

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Abstract

Chromium (VI) is known as a carcinogenic compound, which needs to be removed from drinking water. Nanoparticles of metal oxides have the potential to act as adsorbents for dissolved metal ions. In the current investigation, ZnO nanoparticles were synthesized through a precipitation method. The Nanoparticles were characterized using a combination of SEM and powder X-ray diffraction. Batch studies were performed to investigate the potential binding of cr(VI) to ZnO nanoparticles under light and dark conditions. ZnO is a photoactive material which has the potential to transfer electrons to compounds bound onto the surface of the compound. The effects of pH, time, and temperature were investigated under batch experimentation conditions. In addition, the effect of light on the binding and potential reduction of cr(VI) to cr(III) in solution was investigated. The determination of cr(VI) concentration was performed using the diphenylcarbazide method. In addition, isotherm studies were performed to determine the maximum binding capacity of cr(VI) to the ZnO nanoparticles. The effects of potential interferences on the binding were also investigated, common anions were investigated for the binding of cr(VI). The optimal pH for binding was determined to be pH 2, the binding capacities for cr(VI) were determined were 8.35mg/g, 2.90mg/g and 41.67mg/g, at temperatures of 4, 25, and 45 degrees Celsius.

Methods

ICP-OES : The parameters using for the ICP-OES analysis were as follows:

Parameter	Setting
λ	267.716 nm
RF power	1500 W
Nebulizer	Gemcone (low flow)
Plasma Flow	15 L/min
Auxiliary Flow	0.2 L/min
Nebulizer Flow	0.55 L/min
Sample Flow	1.50 mL/min
Injector	2.0 mm Alumina
Spray Chamber	Cyclonic
Integration Time	10-20 seconds
Replicates	3

Table 1: Operating parameters for the analysis of chromium binding to the ZnO nanoparticles

X-ray Diffraction (XRD):

XRD analysis was performed on a Bruker D2 Phaser Diffractometer. The ZnO adsorbent was analyzed from a range of 5 - 60° in 2θ. With a step size of 0.05 ° with step of count size of 2 seconds per step.

UV-Vis Spectrometer:

Analysis was conducted was conducted in a Perkin Elmer UV/Vis/NIR Spectrometer Lambda 950 from a 450-600nm range. The 1-5 diphenyl carbazide complex with hexavalent chromium is absorbed within that range in UV-Vis spectroscopy.

pH studies

Binding of chromium (VI) ions were tested in a pH range of 2-6. 300 ppb chromium solutions, for both ions, were adjusted using either dilute HNO_3 or dilute NaOH. The pH adjusted samples and controls were performed in triplicate and equilibrated for 1 hour. The samples and controls were centrifuged at 3500 rpm, and supernatants were saved for analysis. The supernatants were analyzed using ICP-OES (Perkin Elmer Optima 8300 DV).

Capacity studies

Binding capacities were determined through experimentation of varying concentration of Chromium (VI) ion metal solutions. Solution concentrations ranged from 3, 30, 100, 300, 1000 ppm and adjusted to optimal binding pH. 10mg of ZnO nanoparticles were placed in a test tube and a 4mL aliquot of pH adjusted chromium containing solution was added. The pH adjusted samples and controls were performed in triplicate and equilibrated for 1 hour. The samples and controls were centrifuged at 3500 rpm, and supernatants were saved for analysis using ICP-OES.

Thermodynamic Studies

Thermodynamic studies were performed at varying temperatures of 4˚C, 23˚C, and 45˚C and determined from the capacity studies, and standard thermodynamic relationships.

Interference Studies

Interference studies were conducted in two separate sets of anions and combination anions. Interfering ion concentrations ranged from 0.3 – 1000 ppm for each set to observe synergistic or antagonistic effect on the binding of Cr(VI) to adsorbent . The Chromium concentration was held steady at 300 ppb for all studies.

Time Studies

The reaction order and rate with respect to both chromium species present in the samples was determined by using in conjunction the ICP-OES to determine the total amount of chromium present and the UV-Vis spectrophotometer to determine the amount of cr(VI) through the complexation with the 1,5-diphenylcarbazide.

Results

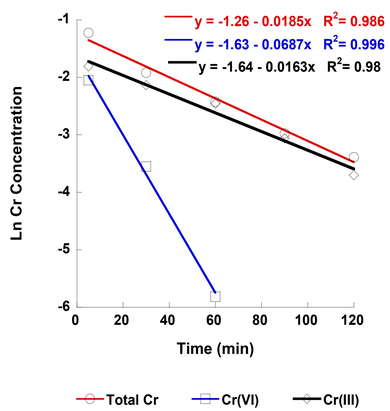

Figure 1: Kinetics under light

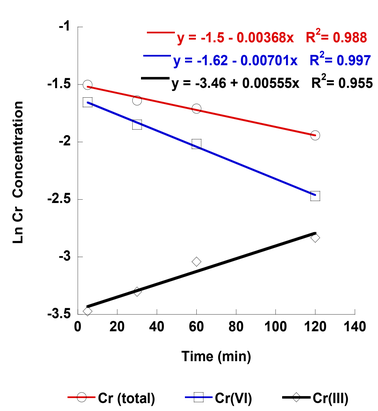

Figure 2: Kinetics under dark conditions

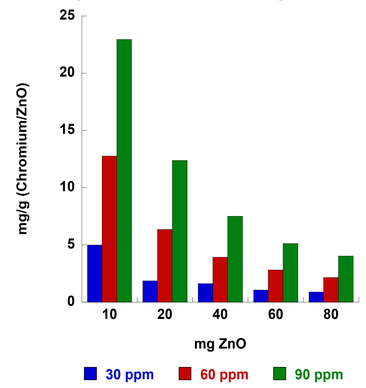

Figure 3: Loading studies under light

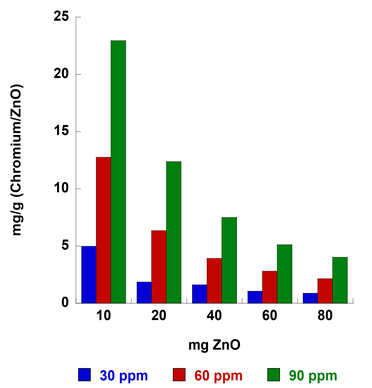

Figure 4: Loading studies under dark conditions

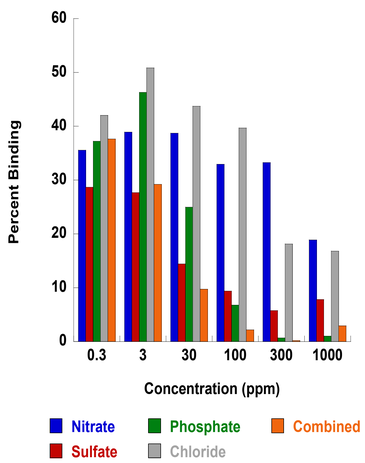

Figure 5: Interference studies

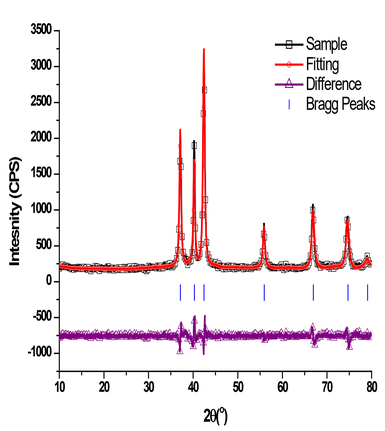

Figure 6: XRD scan of the ZnO nanoparticles

Results

Chromium ion	Equation	Ea (kJ)
Cr(VI)	y = -2551.1x + 5.5264	-21.21

Table 1: Activation energy from an Arrhenius plot

Chromium ion	Equation	R^2	Temperature(°C)	Capacity (mg/g)
Cr(VI)	y = 4357.7x -14.204	R^2 = 0.98	4	8.35
			25	2.9
			45	41.7

Table 2: Binding capacities for the binding of cr(VI) to the ZnO nanoparticles

Chromium Ion	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol)
Cr (VI)	-3.72 (277K) -0.99 (298K) 1.12 (318K)	36.4	-117.9

Table 3: Thermodynamics of the binding of Cr(VI) to the ZnO nanoparticles.

Discussion

pH studies

- At a pH of 2 there was an optimal binding for Chromium (VI).

Capacity studies

- The binding ability of the ZnO nanoparticles as an adsorbent was tested with a series of varying Chromium ion concentrations.
- The gathered data was best fit using the Langmuir Isotherm model.
- The binding capacity was calculated by taking the inverse of the Y intercept from the trend line generated from the plot of chromium binding as a function of varying concentrations of chromium ion.

Thermodynamic studies

- Cr(VI) bound spontaneously within a temperature range of 25-45 ˚C; while Cr(VI) displayed non-spontaneous binding at all recorded temperatures.
- ΔG value, the amount of free energy within the reactions has a stronger correlation to a reaction of equilibrium.

Interference Studies

- Concentrations of 100 -1000 ppm of the anions sulfate and phosphate caused a significant change in binding, which dropped to under 10 percent. Yet 300-1000 ppm of anions caused a slight antagonistic effect.
- For the combination sets, a drastic antagonistic effect was observed between concentrations 30 - 1000ppm.

Loading Studies

- The loading studies were performed under light and under dark conditions, there was no difference between these two conditions. The solutions used were 30, 60, and 90 ppm, there was more mg of chromium bound per g of ZnO for the higher concentration compared to the lower one.
- The amounts of the ZnO nanoparticles used were 10, 20, 40, 60, and 80mg, this determined that 10mg had the highest amount of chromium mg bound per g of ZnO nanoparticles.

Time Studies

- Under light the removal of cr(VI) from solution was greater compared to the samples collected under dark conditions, this was caused by the reduction of cr(VI) to cr(III) with the aid of light.

Acknowledgements

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