Abstract

The study in the thesis aims to develop and test Ca–based nanomaterials precipitating agent and magnetic adsorbents using wet chemical and microwave irradiation methods. The work involves two major technological practices for wastewater treatment: precipitation and adsorption. The experimental studies include: 1) synthesis and characterization of Ca–based ($Ca(OH)_2$, CaO, and CaS) and γ–Fe_2O_3 nanomaterials using wet chemical and microwave irradiation method; 2) evaluation and optimization of their heavy metals removal capability, kinetics and mechanisms toward different nanomaterials via the batch system; 3) integration of the precipitation and adsorption hybrid system as a major technical outcome for the treatment and reclamation of wastewater containing heavy metals (Fe, Cd, Cu, Co, Ni, Pb, and Zn). Different characterization methods have been used to evaluate physicochemical properties of nanomaterials. Lime and lime derived substances have wide industrial application. Traditionally, lime (CaO) or hydrated lime ($Ca(OH_2)$) has also been used for neutralization as well as precipitating agent for wastewater treatment. Calcium sulphide (CaS) is also recognized as precipitating agent in sulfide precipitation and one can achieve a high degree of metal removal compared to hydroxide precipitation. Combination of both hydroxide and sulfide precipitation are also used for wastewater treatment where heavy metals load is quite high. $Ca(OH)_2$ nanoparticles were synthesized by wet chemical method with average size of 35–66 nm. XRD and HRTEM analyses revealed that particles are homogeneous and nearly hexagonal in shape. Nanostructured CaO and CaS was successfully synthesized using a microwave radiation in ambient atmosphere. XRD, FESEM, and HRTEM analyses revealed the presence of face centered cubic structured CaO nanoparticles with 24 nm size and cubic zinc blend type structure of CaS nanoparticles with 18 nm size. Well crystallized nanoscale maghemite tubular structures (150–300 nm in length and 10–25 nm in diameter) have been synthesized by a microwave irradiation method and were found to be superparamagnetic at room temperature.

Optimization of dose depended study to treat heavy metals from simulated wastewater using $Ca(OH)_2$, CaO and commercial lime were performed and $Ca(OH)_2$ nanoparticles showed higher metal removal efficiency compared to CaO nanoparticles and lime. CaS nanoparticles also used as precipitating agent for further reduction of heavy metals after treatment with $Ca(OH)_2$ nanoparticles. Result of combined precipitation showed 99.23-99.80% removal of heavy metals. Magnetic adsorption experiments using γ–Fe_2O_3 nanotubes were carried out by batch experiments to investigate the influence of different factors, such as contact time, initial concentration of metal ions, and pH of the solutions. The isotherm data were well fitted to Langmuir model compared to Freundlich model and the kinetic data of adsorption of heavy metal ions were best described by a pseudo-second-order equation, indicating chemical adsorption. From the Langmuir isotherms, the maximum adsorption capacity of Cu(II), Cd(II), Co(II), Ni(II), Pb(II), and Zn(II) were 111.11, 94.33, 60.60 86.206, 71.42 and 84.95 mg g^{-1}, respectively.

Finally, the integration of precipitation and adsorption techniques was investigated as an alternative hybrid system for continuous treatment of mixed heavy metal from wastewater. Simulated mixed heavy metal wastewater was preliminary treated by combined precipitation method with synthesized $Ca(OH)_2$ and CaS nanoparticles before being subjected to adsorption and magnetic filtration using synthesized γ–Fe_2O_3 nanotubes. Precipitating system demonstrated removal efficiency towards heavy metals and adsorption and magnetic filtration shows high end removal efficiency for heavy metals. This hybrid treatment approach demonstrated a synergetic enhancement for the chemical removal efficiency, and might be able to be employed in a feasible alternative treatment process for heavy metals containing wastewater reclamation

Keywords:$Ca(OH)_2$, CaO, CaS, nanoparticles, γ–Fe_2O_3 nanotubes, Precipitation, Adsorption, Heavy metal removal, Microwave irradiation, XRD, HETRM, FESEM.