Journal of Industrial and Engineering Chemistry 20 (2014) 1285–1292

Contents lists available at SciVerse ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Removal of heavy metals and neutralisation of acid mine drainage with un-activated attapulgite

Thabo Falayi, Freeman Ntuli *

Department of Chemical Engineering, University of Johannesburg, P.O. Box 17011, Doornfontein 2028, Johannesburg, South Africa

ARTICLE INFO

Article history:
Received 23 April 2013
Accepted 2 July 2013
Available online 9 July 2013

Keywords:
Acid mine drainage
Attapulgite
Adsorption
Adsorption isotherms

ABSTRACT

Unactivated attapulgite was characterised and utilised as an adsorbent for the removal of heavy metal and neutralisation of acid mine drainage (AMD) from a gold mine. Adsorption experiments were carried out by agitation of a fixed amount of attapulgite with a fixed volume of AMD in a thermostatic shaker for varying times. Attapulgite showed that it can neutralise acid mine drainage as the pH after 4 h was 7.11. The results showed that metal ion removal after 4 h was 100% for Cu(II) and Fe(II), 93% for Co(II), 95% for Ni(II) and 66% for Mn(II) using a 10% (w/v) attapulgite loading. The experimental data best fit the Langmuir Isotherm with maximum adsorption capacities for Cu(II), Co(II), Mn(II), Fe(II) and Ni(II) being 0.0053, 0.0044, 0.0019, 0.01, and 0.0053 mg/g, respectively. The adsorption process fitted well the pseudo first order kinetics for Co(II) and Cu(II) and pseudo second order for Ni(II), Mn(II) and Fe(II). Thermodynamic data show that Cu(II), Co(II), Fe(II) and Ni(II) adsorption was thermodynamically spontaneous whilst Mn(II) was not thermodynamically spontaneous. The process is endothermic for Cu(II), Co(II), Mn(II), and Ni(II) and exothermic for Fe(II). Spent attapulgite (attapulgite that has already been used to remove metals) could be reused twice without regeneration.

1. Introduction

South Africa suffers from water scarcity as a result of negative water balance (evapotranspiration > rainfall) [1]. This therefore necessitates the need to conserve and protect water sources. Gold mining commenced in the Johannesburg area as early as 1886 [2] and mining exposes large amounts of pyrite and other sulphide minerals to the effects of water and oxygen. This then creates conditions which are favourable to the formation of acid mine drainage (AMD). Acid mine drainage (sometimes also known as acid rock drainage) is acidic water with a pH less than 5.0 laden with iron sulphate and other metals formed when geological strata containing pyrite rock ("fools gold") is exposed to oxidising environments. AMD may contain elevated levels of typical major rock elements like Ca, Mg, K, Na, Fe and Mn as well as heavy metals like Zn, Cu, Cd, Pb, Co, Ni, As, Sb and Se. Composition of AMD varies from place to place. For the Witwatersrand area the pH varies from 2.8 to 6.65, electrical conductivity from 216 to 510 mS/cm, sulphates from 1037 to 4010 ppm, iron from 38 to 1010 ppm, copper 0.03 to 2.948, cobalt 0.0012 to 17.11 ppm, manganese 0.4 to 68.30 ppm and nickel 0.5 to 71 ppm [3,4]. Large scale mine closures in the 1970s within the Witwatersrand and the termination of underground water extraction, has contributed to the acid mine drainage formation in this area [3]. The abandoned voids can be flooded leading to acid mine decanting. This leads to environmental pollution as evidenced by the September 2002 acid mine decant in Mogale/Randfontein area. AMD results in contamination of surface water and contamination of ground water sources. In the western basin of the Witwatersrand, AMD decant has been continuous since August 2002 [5] exceeding the capacity of the infrastructure established to manage it, resulting in untreated water entering the downstream environment via TweelopeSpruit [6]. Attapulgite is a magnesium aluminium phyllosilicate clay with the formula $(MgAl)_2Si_4O_{10}\cdot 4H_2O$ [7]. Attapulgite is a naturally occurring low cost mineral adsorbent. Attapulgite was used for removal of heavy metals and neutralisation of AMD. Most research on AMD has focused on aqueous solution and single metal analysis [7,8], this research paper looks at actual AMD solution which has been fortified. The AMD was fortified as concentrations of Fe, Ni, Cu and Co were below 5 ppm.

2. Experimental

The effect of adsorbent loading, agitation time and temperature on the removal of heavy metals and neutralisation of AMD was

---

* Corresponding author. Tel.: +27 11 559 6003; fax: +27 11 559 6430.
E-mail addresses: fntuli@uj.ac.za, hlekisana@yahoo.com (F. Ntuli).

1226-086X/$ – see front matter © 2013 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jiec.2013.07.007

investigated. Adsorption isotherms, kinetics and thermodynamics were calculated from the data obtained. The ability of attapulgite to immobilise metal ions was also investigated.

2.1. Materials

Acid mine drainage was collected from a local gold mine site and analysed to find the concentration of heavy and other elements present. Un-activated attapulgite was supplied by G&W Base Minerals. Analytical grades of $FeSO_4{\cdot}7H_2O$, $CoSO_4{\cdot}7H_2O$, $CuSO_4{\cdot}5H_2O$, and $NiSO_4{\cdot}6H_2O$ were supplied by Sigma–Aldrich.

2.2. Apparatus

pH and conductivity were measured using Metler Toledo dual meter (Sevenduo pH/conductivity meter with a Metler Toledo InLab Pro ISM pH electrode and Metler Toledo InLab738 ISM conductivity probe). Metal analysis was achieved using an Atomic Absorption Spectrometer (Thermo scientific ICE 3000 Series). XRF (Rigaku ZSX Primus II) was used to analyse for elemental compositions of attapulgite. Fourier transform infrared spectroscopy (Thermoscientific Nicket IS10) was used to characterise attapulgite before and after adsorption experiments. Adsorption experiments were conducted in a thermostatic shaker (Labotec OrbiShaker). A UV–vis spectrophotometer (PG Instruments T60) was used to measure sulphate content.

2.3. Fortification of acid mine drain

To 100 ml of AMD appropriate amounts of sulphate salts of Fe, Co, Cu and Ni were added. The solution was stirred at 200 rpm for 10 min and made up to 1000 ml with raw AMD whilst stirring for a further 20 min. The pH, temperature, conductivity, sulphate content and metal concentration of the collected AMD sample and the fortified AMD sample are shown in Table 1.

2.4. Batch adsorption

2.4.1. Effect of adsorbent dosage

1–10 g of attapulgite was added to different 100 ml solutions of fortified AMD. The solutions were agitated at 200 rpm using a thermostatic shaker maintained at 298.15 K for 4 h. After 4 h, agitation was stopped and the solution pH and conductivity were measured. The solutions were then subsequently filtered using a Buchner funnel and acidified with 1 drop of concentrated nitric acid and stored at 277.15 K awaiting metal analysis using AAS. Sulphate removal experiments were conducted with 10 g attapulgite in 100 ml of AMD solution. Sulphate content was measured using a UV–vis spectrophotometer using Environmental Protection Agency (EPA) method 3754.

2.4.2. Effect of initial concentration

The initial metal concentration of Fe, Cu, Co and Ni were increased to two and three times the concentration values given in Table 4. 100 ml of the resulting AMD solutions was then added to 10 g of attapulgite. The solutions were agitated at 200 rpm using a thermostatic shaker maintained at 298.15 K for 4.0 h. The solutions were then subsequently filtered using a Buchner funnel and acidified with 1 drop of concentrated nitric acid and stored at 4 °C awaiting metal analysis using AAS.

2.4.3. Effect of residence time and temperature

10 g of attapulgite was added to 100 ml of fortified AMD, in a 250 ml conical flask. The initial pH and conductivity, of the fortified AMD were measured. 4 solutions were used and each solution was agitated at 200 rpm using a thermostatic shaker maintained at 298.15 K. The solutions were run for 1, 2, 3, and 4 h, respectively. After each time interval agitation was stopped and the solution was measured for pH and conductivity. The solutions were then subsequently filtered using a Buchner funnel and acidified with 1 drop of concentrated nitric acid and stored at 277.15 K awaiting metal analysis using AAS The amount adsorbed per unit mass of adsorbent at equilibrium q_e is given by

$$q_e = (C_0 - C_e) \times \frac{V}{M} \tag{1}$$

where q_e (mg/g) is the amount of metal adsorbed at equilibrium per unit mass of adsorbent, C_0 (mg/L) is the initial metal concentration in solution, C_e (mg/g) is the equilibrium metal concentration in solution, V (L) is the volume of the solution and M (g) is the mass of adsorbent.

The above procedure was then repeated at 308.15 K and 318.15 K to calculate thermodynamic data.

2.5. Reuse of spent attapulgite

Spent attapulgite (attapulgite that has been used to remove metals form AMD) was dried in an oven at 323.15 K for 12 h. After drying the spent attapulgite was crushed to a fine powder using a mortar and pestle. 10 g of spent attapulgite was then added to fresh fortified AMD and was agitated at 200 rpm using a thermostatic shaker maintained at 298.15 K. After agitation the solution pH and conductivity was measured. The solution was then subsequently filtered using a Buchner funnel and acidified with 1 drop of concentrated nitric acid and stored at 277.15 K awaiting metal analysis using AAS. This spent attapulgite was re used two times following the outlined procedure. In total the attapulgite was used in three different treatment cycles.

2.6. Theory

2.6.1. Adsorption isotherms

To study the thermodynamic behaviour of the adsorption process, adsorption isotherms were used. In order to find the adsorption capacities of the metals adsorbed by attapulgite, the experimental results were analysed using the Langmuir (Eq. (2)) and Freundlich (Eq. (3)) isotherms. The following linearised equations were used for this purpose

$$\frac{C_e}{q_e} = \frac{1}{q_m \cdot b} + \frac{C_e}{q_m} \tag{2}$$

$$\log\ q_e = \log\ K_F + \frac{1}{n}\ \log\ C_e \tag{3}$$

where C_e (mg/L) is the metal concentration in solution at equilibrium q_e (mg/g) is the amount of metal adsorbed per unit mass of adsorbent, q_m (mg/g) is the maximum adsorption, b (L/g) is

Table 1
Temperature, pH, conductivity, sulphates and metal parameters of raw and fortified AMD.

Parameter	Reading (raw AMD)	Reading (fortified AMD)
pH	2.66	2.84
Temperature (°C)	23.4	23.3
Conductivity (mS/cm)	2.62	5.77
Sulphates (ppm)	2820	3522
Fe (ppm)	4	532
Mn (ppm)	120	114
Ni (ppm)	Below detection limit	20.35
Cu (ppm)	Below detection limit	15.65
Co (ppm)	Below detection limit	21.25