Synthesis Of MoS₂-Based Nanohybrid For Effective Removal Of Mercury From Aqueous Solution **S**

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Abstract

In this study SH-MWCNTs/MoS2 nanohybrid was synthesized via hydrothermal method. The nanohybrid composite was then characterized using the fourier transform infra-red (FTIR) spectroscopy, scanning electron microscopy (SEM) and Energy-dispersive x-ray spectrometry (EDS) then the successful incorporation of relevant binding groups was confirmed. The synthesized adsorbent was then used for the removal of Hg^{2+} ion from aqueous solution and its adsorption behavior and capacity determine using the kinetic models. It was that Hg^{2+} ion uptake onto SH-MWCNTs/MoS₂ nanohybrid composite occurred through chemisorption mechanism, achieving and adsorption capacity of 0.9661 mg/g. The SH-MWCNTs/MoS₂ nanohybrid nanocomposite therefore showed potential for the removal of Hg2+ ion from contaminated water.

Keywords: Mercury, water pollution, ASM, SH-MWCNTs/MoS2 nanohybrid, adsorption

Introduction

Artisanal and small-scale mining is livelihood activity of considerable economic importance in developing countries, supporting the lives of millions of people across Africa, South America and Asia. One of the most recorded ASM activity is goldmining, which takes place through soil excavation and gold extraction from the soil. Mercury is used for the extraction of gold from the soil in a process called amalgamation which is considered as a cheap and reliable way of gold recovery from low-grade ore (Spiegel 2009). It is however reported that the rudimentary practice of mineral extraction during artisanal and small-scale gold mining contributes to the emission of 1000 tonnes of mercury into the environment every year (Swain et al. 2007). Mercury is known as a very toxic element that can pose a serious threat to the life of humans, animals and other ecological entities (Zabihi et al. 2009). River pollution by mercury from ASM activities generally occurred in remote, poor and rural areas where access to safe and clean water is a challenge, compelling the community to rely on untreated water sources for their various needs. Such communities require a facile and affordable technology such as adsorption to treat their water; few adsorbents have been tested for the removal of mercury from water, ranging from grafted polymer cellulosic materials to surfactant impregnated clayish materials which all suffer a number of disadvantages including lower adsorption capacities, instability and lower affinity for mercury.

Carbon nanotubes have shown remarkable performance as adsorbent because of their intraparticle porosity, large surface area and sufficient stability during regeneration; while on the other hand Sulphur has been demonstrated to have high affinity for mercury. In the context of this study, mercapto propyl trimetoxysilane (3-MPTES) was grafted to multi-wall carbon nanotubes to form the composite SH-MWCNTs which was then used to synthesize SH-MWCNTs/ MoS₂ nanohybrid composite with the aim to develop an effective adsorbent with high affinity for mercury and can be used to treat

water contaminated with mercury; to the best of our knowledge, this the first time such composite has been tested for the removal of mercury from water.

Methods

Preparation of SH-MWCNTs/MoS2 nanohybrid composite

The first step consisted of the grafting propyl trimethoxysilane of mercapto (3-MPTES) on multi-walled carbon nanotubes (MWCNTs) resulting in the of SH-MWCNTs that formation was reacted with sodium molybdate to form SH-MWCNTs/MoS, through hydrothermal method (Fosso-Kankeu et al., 2018).

Characterization of the adsorbent

The synthesized adsorbent was pulverized using the pestle and mortar to form a powder samples suitable for analysis by the SEM and FTIR. The IRAffinity-1S Fourier transform infrared spectrophotometer from the University of Johannesburg was used with a spectral range of 4000 to 500 cm⁻¹. The JEM-2100 multipurpose electron microscope was used for the SEM-EDS characterization. The magnification for the SEM image was set at 10 μ m.

Adsorption experiments

Batch equilibrium sorption experiments were carried out at different time intervals (10, 15, 30, 50, 60 and 70 mins) with fixed Hg concentration (2 mg/L) in 100 mL glass bottle with blue screw cap, adsorbent dose (SH-MWCNTs/MoS2 nanohybrid) 0.05g, shaking speed of 200 RPM and total volume of Hg²⁺ solution was kept 10 mL in a rotary shaker. These experiments were performed at pH6.

After the sorption equilibrium was reached (60 min), the solution was separated from the adsorbent by Millipore membrane filtration. The initial and equilibrium Hg²⁺ ion concentrations in each bottle were determined by ICP-OES.

Results and discussion

Physico-chemical properties of the adsorbent FTIR

The FTIR spectrum showed predominant peaks at 2917, 1617, 1521, 1441, 1109, 739

and 675 cm⁻¹ which corresponded to the presence of the following functional groups: H-C-H assymetric, C-C=C symmetric stretch, C-C=C asymmetric stretch, C-O stretch, C-H rock and C-H bend respectively; these are suitable groups to interact with and bind to Hg2+ ion in solution.

SEM analysis

The EDS spectrum (Fig. 2a) shows the presence of elements such as C, Si, S, Na and Mo which are primary components of mercapto propyl trimethoxysilane (3-MPTES), multi-walled carbon nanotubes (MWCNTs) and sodium molybdate, therefore indicating that all the compounds were effectively incorporated in the composite and the synthesis was successful. The SEM image (Fig. 2b) recorded at 10 μ m shows an homogeneous distribution of small bead of large surface area suitable for the adsorption of metal.

Adsorption kinetic studies

The kinetic studies were performed by collecting and analyzing the samples at the predetermined time interval (10 min) until the consecutive residual Hg^{2+} ion concentrations became closer. The kinetic data for the adsorption of Hg^{2+} ion onto nanohybrid at 5 mg/L Hg^{2+} ion concentration were tested with the well-known kinetic models namely pseudo first order model and pseudo second-order model. The parameters of these kinetic models are provided in Table 1 and the graphs are plotted in Figure 3.



Figure 1 FTIR spectrum of the synthesised nanocomposite



Figure 2 (a) SEM image and (b) EDS plot of the synthesized nanohybrid

Pseudo-first-order and pseudo-second-order kinetic equations

The pseudo-first-order kinetic (Eq. (2)) (Lagergren, 1898) and the pseudo-second order kinetic (Eq. (3)) models (Ho and McKay, 1998) were most often used to govern the rate constant and to examine the mechanism of the adsorption process. The linear forms of namely pseudo-first-order and pseudo-second-order kinetic models are expressed as follow:

$$\frac{\log(q_e - q_t)}{q_e} = \log q_e - \frac{k_1}{2.030}$$
(2)

$$\frac{t}{q_t} = \frac{1}{k' q_e^2} + \frac{t}{q_e}$$
(3)

where qe (mg/g) is the adsorption capacity of the nanohybrid at equilibrium; K1 (min-1) is the rate constant of the pseudo-firstorder model; and K'(g mg⁻¹ min⁻¹) is the rate constant of the pseudo-second-order model.

From the effect of time on the adsorption of Hg^{2+} ion onto nanohybrid. It was apparent that the adsorption of Hg^{2+} ion is a timedependent process. The adsorption occurred very rapidly within the initial 50 min, in which \approx 95% adsorption of Hg^{2+} ion was achieved. Such rapid adsorption can be possibility because of a great number of various functional groups observed in Fig. 1 on to the surface of SH-MWCNTs/MoS2 and because of the high porosity and high surface area existing in MWCNTs, while the presence of sulphur in Nanohybrid also support the process of Hg²⁺ adsorption, because sulphur is well known to have high affinity for mercury. At the same time, the adsorption of Hg₂₊ ion well fitted the pseudo-second-order kinetic equation (Figure 3); the correlation coefficient ($R^2=0.999$) is close to 1, the rate constant (K' (g.mg-1.min-1) was calculated to be 2.53. This therefore implies that the adsorption of Hg2+ ion onto SH-MWCNTs/ MoS2 is dominated by a chemisorption mechanism (Fosso-Kankeu et al. 2016a, b; Fosso-Kankeu et al. 2017; Leudjo Taka et al. 2018) attributed to the interaction of binding groups including Sulphur at the surface of the adsorbent with Hg2+ ion.

Conclusion

The present work revealed the feasibility of using new adsorbent (SH-MWCNTs/MoS₂ nanohybrid) for the removal of Hg^{2+} ion from aqueous solutions. The efficiency of Hg^{2+} ion

Table 1 Different parameters of Adsorption kinetics of Hg²⁺ onto SH-MWCNTs/MoS, nanohybrid

Kinetics models	Parameters	Values
Pseudo-second-order	qe (mg.g ⁻¹)	0.9661
	K' (g.mg ⁻¹ .min ⁻¹)	2.5311
	R ²	0.999
Pseudo-first-order	qe (mg.g ⁻¹)	0.1539
	K1 (min ⁻¹)	8.75 x 10 ⁻³
	R ²	0.9115



Figure 3 Adsorption kinetics of Hg2+ onto SH-MWCNTs/MoS2 nanohybrid according to (a) Pseudo-firstorder model, and (b) pseudo-second-order model

removals was found to be greater than 95% at 5mg/L by using nanohybrid. The adsorption behavior is well described by pseudo-secondorder kinetic and Sips isotherm models. The best behavior of adsorbent for retaining elemental mercury because of their (i) high sulphur content, (ii) large surface area, and (iii) large total pore volume, especially a large micropore volume, where the potential for interaction between the solid sorbent and mercury molecules is substantially greater than that in the wider pores.

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