

## Performance of synthesized hybrid hydrogel nanocomposite applied for the removal of metal ions from aqueous solutions

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### Abstract

The removal of metal ions from mine effluents by a copolymerized gelatine (GL-cl-PAAm) and the hybrid hydrogel nanocomposite was investigated in the present study. Both adsorbents were characterized using fourier transformed infra-red spectrometer (FTIR) and their adsorption behaviour was studied through the determination of the effects of adsorbent dosage and temperature on the adsorption capacity. The thermodynamic study at 20, 30 and 40°C showed that the adsorption process using GL-cl-PAAm and the hybrid hydrogel nanocomposite were both exothermic ( $\Delta H = 351 \text{ KJ/mol} > 0$  and ( $\Delta H = 17.71 \text{ KJ/mol} > 0$ , respectively) while the values of the Gibbs free energy ( $\Delta G < 0$ ) for both adsorbents was negative indicating that for the initial concentrations of Cd considered, the adsorption process was of a spontaneous nature. The adsorbents were found to effectively remove uranium (U), nickel (Ni) and lead (Pb) from mine effluents achieving a maximum removal of 100%. The developed adsorbents have shown the potential to remove metals in synthetic and complex solutions.

Key words: Clinoptilolite, hybrid hydrogel nanocomposite, adsorption, mine effluent, thermodynamic

### Introduction

Hydrogels also referred to as hydrophilic gels are network of polymer chains with the ability to adsorb water arising from hydrophilic functional groups attached to the polymeric backbone. They have a wide range of applications in food industry, bioengineering, biomedicine and water treatment processes. Hydrogels made from biopolymers are renewable, safe and can be afforded at relatively low cost; they can be easily modified through biochemical and chemical mechanisms, making them suitable for the synthesis of composites. During synthesis of hydrogels important consideration must be taken to ensure that the polymer does not dissolve, this is done by systematic introduction of cross-links, several methods have therefore been developed for preparation of suitable hydrogels (Park et al. 1993). Akhtar et al. (2015) have identified the physical cross-linked gels and the chemical cross-linked gels as the major methods for synthesis of hydrogels. The physical cross-linked gels can be achieved by hydrogen bonds, amphiphilic graft and block polymers, crystallization, ionic interaction and protein interaction (Yokoyama et al. 1986; Gacesa 1988; Mathur et al. 1998; Forster and Antonietti 1998; Miyata et al. 1999); the chemical cross-linked gels is done by complementary groups chemical reaction, high energy radiation, free radical polymerization and by the use of enzymes (Sperinde and Griffith 1997; Martin et al. 1998; Coviello et al. 1999; Ray et al. 2010; Amin et al. 2012; Zu et al. 2012; Fosso-Kankeu et al. 2015). Hydrogels have been filled with other adsorbents to add new properties to the natural polymers such as to improve its adsorption capacity. According to Jing et al. (2013) hybrid hydrogels have three major advantages over their components, these include: biological materials introduced into the hybrid hydrogels can lower the cost of the resulting composite; the composite being made of different materials results into hydrogels with various active groups and remediation potentials, therefore capable to remove more than one contaminants from polluted water (Im et al. 2010; Yun et al. 2010; Tang et al. 2010; Rao et al. 2011); finally hybrid hydrogels have good

mechanical properties and tolerance to vigorous stirring (Pan et al. 2008; Chatterjee et al. 2010). Hydrogels have been effectively used for the removal of pollutants from water; Mandal et al. (2012) prepared a semi-IPN (interpenetrating polymer network) and IPN based on poly(vinyl alcohol) and poly(AA-co-2-hydroxyethyl methacrylate) with various compositions that they used for removal of rhodamine B and methyl violet from solution; they observed that the sorption capacity of both dyes increased with the increase of the copolymer content in the gel. In a separate study, semi-IPN composite hydrogels prepared by the incorporation of cellulose derivatives in a matrix of poly(methacrylamide) was used by Chauhan and Mahajan (2002) for the removal of  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cr}^{6+}$  from solution and they found that the functional groups on the gels have a considerable impact on their adsorption capacity and mechanism.

Metals found in surface water have an influence on the aquatic life as well as human; when these contaminated sources are used for irrigation or domestic purposes the metal pollutants can negatively affect the health of people consuming the water and the crops. It is therefore important to use a sustainable method such as adsorption to effectively remediate water pollution (Fosso-Kankeu et al. 2011; Mittal et al. 2013; Fosso-Kankeu et al. 2016a, b).

This study investigates the characteristics of a zeolite-hydrogel composite and its potential as adsorbent for the treatment of acid mine water.

## Methods

### Water samples

Water samples from the mine effluent were collected from mine dams in the Mpumalanga and the North-West provinces of South Africa. A polypropylene plastic bottle of a capacity of 500 mL was used to collect the water at the subsurface of the dams; the physicochemical parameters of the water samples such as pH, electrical conductivity, oxido-redox potential and temperature were determined in situ using a portable Lovibond SensoDirect 150 multi-parameter water quality pH meter. The samples were then stored in cooler box containing ice packs and transported in the laboratory for further analyses.

### Synthesis of adsorbents

GL, acrylamide (AAm), N,N-methylene-bis-acrylamide (MBA), potassium persulfate (KPS) were purchased from Sigma-Aldrich, South Africa. Clinoptilolite was obtained from a local company in South Africa.

GL-cl-PAAm and hybrid hydrogel composite were synthesized using the free radical graft copolymerization technique. For the synthesis of GL-cl-PAAm hydrogel, initially GL (1 g) was dispersed in 20 mL deionized water and stirred vigorously followed by the addition of KPS (20 mg) and MBA (30 mg). 1 g AAm was added in the reaction vessel and stirred again. Finally, the reaction temperature was maintained at 60 °C and the reaction was allowed to proceed for 2 h without any further disturbance. After, the completion of reaction, the reaction vessel was allowed to cool down at room temperature. The homopolymer, unreacted monomers and the crosslinkers were separated by repeated washings with hot water followed by acetone. Finally, the synthesized hybrid hydrogel composite was dried in hot air oven for 24 h and powered using the ball mill.

For the synthesis of hybrid hydrogel composite, initially, 20 mg clinoptilolite was dispersed in 20 ml deionized water by sonicating the solution for 2 h using the ultrasonicator, thereafter, the same procedure used to synthesize the GL-cl-PAAm hydrogel was followed.

### Characterization

The graft co-polymerization of the PAAm onto GL and the effect of the incorporation of Clinoptilolite within the hydrogel polymer matrix on its physico-chemical properties were studied using FTIR. The FTIR of samples were recorded on the Perkin-Elmer Spectrum 100 spectrometer (USA) using the KBr pellet method in the spectral range 4000–400  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

### Adsorption experiments

The adsorption behavior of the GL-cl-PAAm and the hybrid hydrogel composite for the adsorption of metal ions was studied in batch mode. Initially, the varied mass of the adsorbents were added in the metal ion solutions taken in plastic bottles. The bottles were agitated on a thermostatic water bath shaker (Labcon, South Africa) for 1 h. After the completion of the adsorption experiment, the bottles were removed from the water bath shaker. The solutions were filtered using syringe filters and the concentration of remaining metal ions in the solution were measured using an inductively coupled plasma optical emission spectrometer (ICP Expert II, Agilent Technologies 720 ICP-OES). The percentage adsorption was calculated using Eq. (1) (Mittal et al. 2015; Mahdavinia et al. 2013).

$$\% \text{ Adsorption} = \frac{(C_o - C_e)}{C_o} \times 100 \tag{1}$$

Where,  $C_o$  and  $C_e$  are the initial and equilibrium concentrations (mg/L) of the metal ion, respectively. The investigation of the effect of temperature on the adsorption potential of adsorbents was done by varying the temperature between 20, 30 and 40°C while keeping the other parameters constants.

### Results and discussion

#### Characterization of the clinoptilolite and the hybrid hydrogel composite

The FTIR spectra of the clinoptilolite and hybrid hydrogel composite are shown in Figure 1. The FTIR of clinoptilolite has shown the characteristic peaks of the hydrated water at 3610 and 1641  $\text{cm}^{-1}$ , these bands were due to the water molecules associated with Na and Ca in the channels and cages of clinoptilolite structure. Some other peaks were observed at 1178  $\text{cm}^{-1}$ , due to the asymmetric stretching vibration modes of internal T-O bonds in  $\text{TO}_4$  tetrahedra (T=Si and Al), 786 and 694  $\text{cm}^{-1}$ , due to the stretching vibration modes of O-T-O groups and the bending vibration modes of T-O bonds, respectively (Vasylechko et al. 2003; Korkuna et al. 2006). On the FTIR spectrum of the hybrid hydrogel composite, the characteristic peaks of clinoptilolite at 1601, 786 and 615  $\text{cm}^{-1}$  were observed along with the peaks at 3455  $\text{cm}^{-1}$ , due to the -OH stretching vibrations, 2929  $\text{cm}^{-1}$ , due to the aliphatic -CH<sub>2</sub> stretching vibrations, 1713  $\text{cm}^{-1}$ , due to the C=O stretching in AAm, 1449  $\text{cm}^{-1}$ , due to the amide -NH in-plane bending and 1173  $\text{cm}^{-1}$ , due to the amide -CN stretching vibration. The presence of the characteristic peaks of the clinoptilolite as well as the characteristics peaks of the AAm in the FTIR of the hybrid hydrogel composite confirm the successful grafting of AAm onto the GL as well as the incorporation of clinoptilolite within the hydrogel polymer matrix.

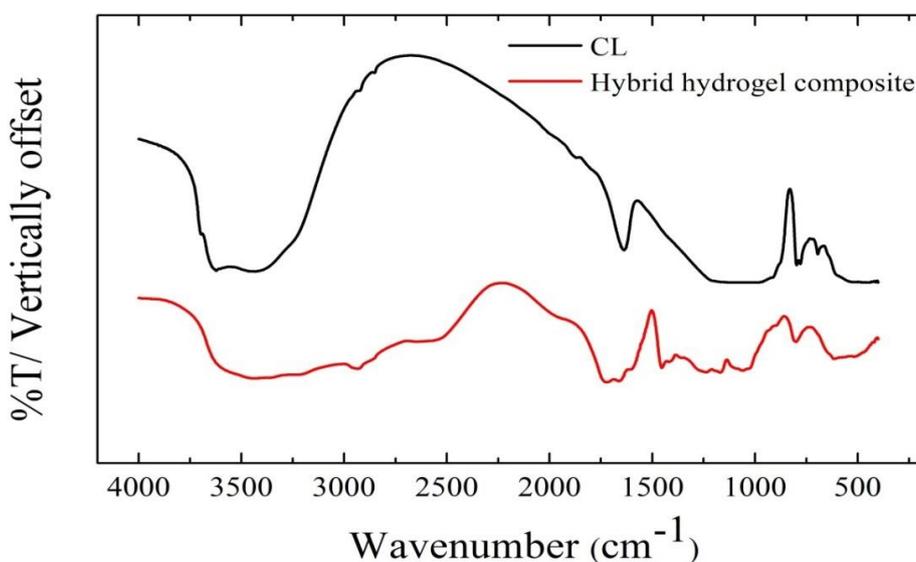


Figure 1 FTIR spectra of clinoptilolite and the hybrid hydrogel composite

### Effect of the adsorbent dosage

The effect of the adsorbent dose on the adsorption efficiency of the GL-cl-PAAm and the hybrid hydrogel composite was investigated with varied mass of the adsorbents (25-150 mg) and the results are depicted in Figure 2. It was observed that for both the adsorbents the adsorption efficiency increased with increasing polymer dose and attained the optimum value beyond which no noticeable increase in the adsorption efficiency was observed with further increase in the dosage of adsorbents. The adsorption efficiency increased initially due to the availability of more adsorption sites with increased mass of the adsorbent. The saturation in the adsorption efficiency at much higher mass of the adsorbents was due of the fact that, with higher amounts of the adsorbents, the total available surface area decreased through the aggregation of adsorption sites and the increased diffusion path (Mittal et al. 2015; Mittal et al. 2016).

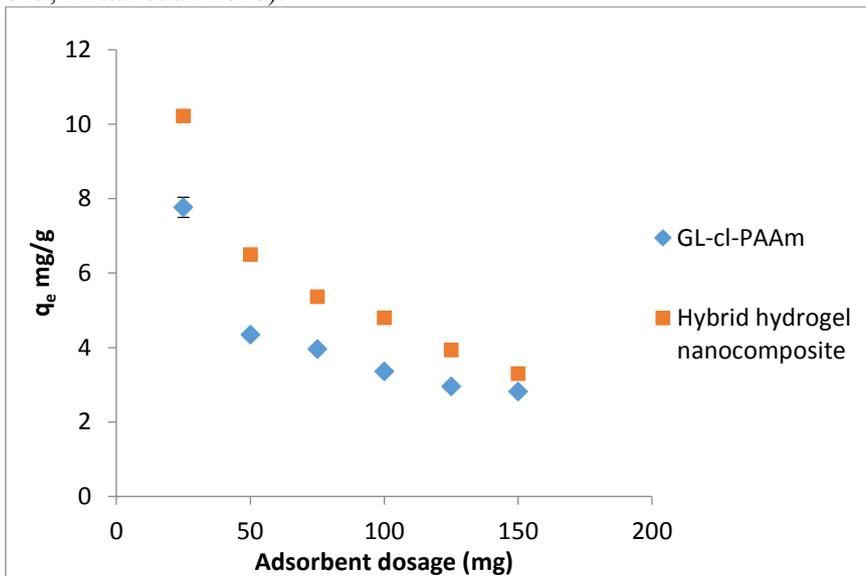


Figure 2 Adsorption of cadmium at various dosages of GL-cl-PAAm and hybrid hydrogel composite

### Thermodynamic study

To determine the temperature dependency of cadmium removal from solution, adsorption experiments were carried out at three different temperatures (20, 30 and 40°C). An increase of adsorption was observed from 20°C to 30°C, follow by a sudden decrease at 40°C. Metal ions removal is strongly dependent on solution temperature, similar trend was observed by several researchers (Kula et al. 2008; Karami 2013; Abdelwahab et al. 2015) who explained this phenomenon as a result of the exothermic nature of the adsorption; furthermore, adsorption mainly occurs through electrostatic interaction which is usually associated with low adsorption heat (Karaca et al. 2006). The thermodynamic behaviour of the adsorption of cadmium onto GL-cl-PAAm and the hybrid hydrogel nanocomposite was investigated through the determination of parameters such as the standard free energy change known as Gibbs free energy ( $\Delta G^\circ$ , KJ mol<sup>-1</sup>), entropy change ( $\Delta S^\circ$ , J mol<sup>-1</sup> K<sup>-1</sup>) and enthalpy change ( $\Delta H^\circ$ , KJ mol<sup>-1</sup>) (Table 1). The Gibbs free energy ( $\Delta G^\circ$ ) for the adsorption of cadmium onto GL-cl-PAAm and the hybrid hydrogel nanocomposite was calculated using the van't Hoff equation below:

$$\ln K_a = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{2}$$

Where  $K_a$  ( $q_e/C_e$ ) is the equilibrium constant or the linear adsorption distribution coefficient, T is the solution temperature (K), and R is the gas constant (8.314 x 10<sup>-3</sup> KJ mol<sup>-1</sup> K<sup>-1</sup>).

The values of  $\Delta S^\circ$  and  $\Delta H^\circ$  were obtained from the intercept and slope of the plot  $\ln K_a$  vs  $1/T$ , these values are shown in Table 1. The negative value of  $\Delta G^\circ$  indicates the spontaneous nature of the adsorption of cadmium onto GL-cl-PAAm and the hybrid hydrogel nanocomposite; while the values of  $\Delta S^\circ$  and  $\Delta H^\circ$  were both positive. The positive value of  $\Delta S^\circ$  suggests increased randomness at the

solid/liquid interface with some structural changes obtained in the adsorbate and adsorbent system (Onal et al. 2006; Hiwarkar et al. 2015). The positive value of  $\Delta H^\circ$  confirms the endothermic nature of the process.

**Table 1** Thermodynamic parameters for the removal of cadmium from solution

Adsorbent	Kc	Temp	$\Delta G$ (KJ/mol)	$\Delta S$ (J/mol/K)	$\Delta H$ (KJ/mol)
GL-cl-PAAm	1.620974	293.15	-1177.25814	2914.72	43.36
	1.630947	303.15	-1232.87589		
	1.635984	313.15	-1281.57248		
Hybrid hydrogel nanocomposite	5.85189	293.15	-4306.0458	148.06	0.34
	5.314635	303.15	-4210.22016		
	5.033183	313.15	-4207.43968		

**Removal of metal pollutants from mine effluents**

Surface waters were collected around mines in Orkney (mine effluent A) and Clewer (mine effluent B) located in the North West Province and the Mpumalanga Province of South Africa. Analysis of the water quality (Table 2) showed that the mine effluent A was less polluted; with pH close to neutral and conductivity within the guideline value; however metal ions such as  $U^{+6}$ ,  $Fe^{+2}$ ,  $Ni^{+2}$  and  $Pb^{+2}$  occurred in relatively high concentrations exceeding the recommended values in the guideline (SABS, 2005). The mine effluent B on the other side was highly polluted, a typical acid mine drainage (AMD), characterized by acidic pH (~2.5), abnormal conductivity and very high concentrations of metals (Table 2) such as  $U^{+6}$ ,  $Cd^{+2}$ ,  $Co^{+2}$ ,  $Fe^{+2}$ ,  $Ni^{+2}$ ,  $Pb^{+2}$  and  $Zn^{+2}$  which exceeded the recommended values in the guideline (SABS, 2005).

**Table 2** Physicochemical characteristics of mine effluents

Parameters	Unit	Recommended value SABS (2005)	Samples	
			Mine effluent A	Mine effluent B
pH		5 – 9.5	7.74	2.55
Eh	mV	NA	-42	216
EC	mS/cm	< 150	3.36	6.55
Sulphate	mg/L	< 400	1360	7035
Chloride	mg/L	< 200	180	400
Nitrate	mg/L	< 10	8.5	123.2
Cyanide	mg/L	< 0.050	65	242
Cd	mg/L	< 0.005	nd	0.45
Co	mg/L	< 0.5	nd	12.18
Fe	mg/L	< 0.2	0.24	2516.72
Mn	mg/L	< 0.1	4.92	104.86
Ni	mg/L	< 0.15	nd	13.06
Pb	mg/L	< 0.02	1.26	43.57
U	mg/L	NA	0.41	2.378
Zn	mg/L	< 5	nd	8.82

The synthesized adsorbents were used to remove metal ions from mine effluents A and B. The results in Table 3 show that the adsorbents performed relatively well for the removal of metals in mine effluent A, achieving a total removal of  $U^{+6}$ ,  $Fe^{+2}$ ,  $Ni^{+2}$  and  $Pb^{+2}$ . On the other hand only  $Co^{+2}$ ,  $Ni^{+2}$  and  $Pb^{+2}$  were removed above 80% in mine effluent B. There was no major difference observed when the solution temperature was varied from 25°C to 45°C; the adsorption performance in this case varied

with the metal ions as some metal ions were easily removed at high temperature while the others were poorly removed at such temperature.

**Table 3** The concentrations of different metal ions in the mine effluents before and after adsorption

Metal solution	in	Concentration mg/L							
		Mine effluent A				Mine effluent B			
		Before adsorption	Fitness	After adsorption	Fitness	Before adsorption	Fitness	After adsorption	Fitness
U <sup>+6</sup>		0.41	No	0	Yes	2.38	No	0.83	No
Cd <sup>+2</sup>		0	Yes	0	Yes	0.45	No	0.18	No
Co <sup>+2</sup>		0	Yes	0	Yes	12.18	No	1.44	No
Fe <sup>+2</sup>		0.24	No	0.14	Yes	2516.72	No	2260	No
Ni <sup>+2</sup>		1.52	No	0	Yes	13.06	No	1.10	No
Pb <sup>+2</sup>		1.26	No	0	Yes	43.57	No	2.58	No
Zn <sup>+2</sup>		0	Yes	0	Yes	8.82	No	7.59	No

Overall the hybrid hydrogel composite performed better than the GL-cl-PAAm and the performance of the former was considered to evaluate the suitability of the treated water. After treatment it was found that metal ions such U<sup>+6</sup>, Fe<sup>+2</sup>, Ni<sup>+2</sup> and Pb<sup>+2</sup> initially present at unacceptable concentrations in mine effluent A were reduced to acceptable values based on the SABS guideline (2005); while the concentrations of all the metal ions in mine effluent B remained unacceptable after treatment; such solution requires a pretreatment process prior to the application of our adsorbents.

### Conclusions

The hybrid hydrogel nanocomposite was successfully synthesized in this study as demonstrated by the FTIR results; the developed adsorbent was found to perform better than its components at relatively high temperature. The adsorption process occurred through an endothermic and spontaneous reaction. The application of the newly developed adsorbent for the treatment of mine effluent resulted into the total removal of trace metals from solution while the major metals were not totally removed. The developed adsorbent can therefore play a role of polishing to complement a treatment method applied upstream.

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