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Thermodynamic properties and adsorption behaviour of hydrogel nanocomposites for cadmium removal from mine effluents

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ABSTRACT

This research paper reports on the utilization of the hydrogel of gelatine (GL) and its hybrid nanocomposite with clinoptilolite for the adsorption of Cd^{2+} ions from an aqueous solution and multi-metal ions from mine effluents. The hydrogel was synthesized using the graft co-polymerization of acrylamide (AAm) onto GL and the hybrid hydrogel nanocomposite was prepared by incorporating clinoptilolite within the hydrogel matrix. The synthesized polymers were characterized using different characterization techniques such as FTIR, XRD, SEM and TGA. The adsorption behaviour of the synthesized adsorbents for the adsorption of Cd^{2+} was studied using different adsorption parameters such as pH, temperature and adsorbent dosage. Adsorption kinetics followed the pseudo-second-order rate equation, whereas, the adsorption isotherm followed both the Freundlich and Langmuir isotherm models. The thermodynamics studies revealed that the adsorption processes were spontaneous and endothermic in nature. Moreover, the synthesized adsorbents were also successfully utilized for the adsorption of different metal ions from the mine effluents.

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Introduction

Water related problems are exacerbated by pollution mainly from the industries which contribute significantly to the release of potentially toxic metals in surface and ground waters. Among these industries, the mining and metallurgical sectors have played major roles in the contamination of the water resources, impacting directly through the release of metals loaded effluents in the river network or indirectly by disposing solid waste containing residual metals in the environment. These mine tailing dumps weather over time, accelerating the mobility of metal ions which are then continuously released into the surface and ground water. Some metal ions such as Pb^{2+} and Cd^{2+} can negatively affect the aquatic biota and human health even at relatively low concentration [1]. The removal of these metal ions from large and diluted environmental solutions require effective and sustainable techniques. A number of techniques developed over the years have shown patchy performance, as they ensure the removal of metal ions from solution but at very high cost while contributing at the same time to the formation of waste by-products. The adsorption technique has emerged as one of the inexpensive and eco-friendly technique which requires minimum skill for implementation [2–7]. A host of sorbents has been successfully applied for the removal of metal ions from waste water, but the bio-sorbents are preferred because of their unique properties such as biodegradability,

low-cost and abundant availability [4,7]. Typical examples of bio-sorbents are hydrogels deriving from biopolymers which can be produced from a wide range of materials including gums, collagen, cellulose, alginate, carrageenan and chitosan [8–12]. Polysaccharides based hydrogels are attractive because they are biodegradable and biocompatible and have been successfully applied for the removal of organic and inorganic pollutants from aqueous solutions [8,11–14].

The adsorption behaviour of biopolymer based hydrogels can be improved in several ways i.e. by incorporating any other foreign material such as metal oxide nanoparticles, zeolites or clays within the polymer matrix [10,11,15–17]. Some natural zeolites and clays such as bentonite and clinoptilolite are inexpensive and have been used extensively in water purification applications [17–23]. The sieve-molecular properties of zeolites and the presence of strongly

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active surface sites make them very useful for the adsorption of different kinds of pollutants from wastewater [16,18,19,22,24]. Clinoptilolite is a natural mineral composed of an aluminosilicate matrix which can incorporate a variety of metal oxides and metal cations [25,26]. They have been previously used for the adsorption of different dyes and metal ions from the wastewater [18,19,22,24].

The focus in this study was to develop a sustainable sorbent with a high and predictable adsorption capacity, capable to function effectively under natural environmental conditions. Therefore, keeping in view the extraordinary properties of biopolymers and clinoptilolite, in this particular research work a hydrogel and hybrid hydrogel composite of gelatine (GL) and clinoptilolite were synthesized using the free radical graft co-polymerization technique. In addition to the general properties of biopolymers mentioned above, gelatine is non toxic and has high water solubility and a net negative charge with the —NH_2 and —COOH functional groups suitable for the adsorption of cations. In the hydrogel, gelatine can enhance hydrophilicity, gel strength as well as functional properties [27,28]. The synthesized materials were used for the adsorption of Cd^{2+} ions from the aqueous solution. Furthermore, the synthesized adsorbents were utilized for the removal of different metal ions from the mine effluents; to the best of our knowledge, it is the first time the adsorption behaviour and capacity of gelatine based hydrogel is tested in the treatment of a complex solution such as mine effluent. The enhancement in the adsorption performance of the hydrogel after the incorporation of clinoptilolite was explained on the basis of the different structural and morphological changes observed by characterization techniques.

Experimental

Reagents and water samples

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. To prepare the synthetic solution of cadmium at various concentrations, an analytical grade salt of $Cd(NO_3)_2.4H_2O$ from Associate Chemical Enterprises (ACE South Africa) was used. To vary the pH the chemicals used included hydrochloric acid (HCl) 32% and sodium hydroxide (NaOH) 32%, all analytical grade and purchased from ACE South Africa.

Water samples from the mine effluents studied were collected from mine slimes 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 (Table 1) using a portable Lovibond SensoDirect 150 multi-parameter water quality pH meter. The samples were then stored in a cooler box containing ice packs and transported to the laboratory for further analyses.

Synthesis of adsorbents

The GL–cl–PAAm and the hybrid hydrogel composite were synthesized using the free radical graft co-polymerization technique. For the synthesis of the 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). One gram of 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 cross linkers 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 powdered using the ball mill.

For the synthesis of the 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 was followed which was used to synthesize the GL–cl–PAAm hydrogel.

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 different characterization techniques such as FTIR, XRD, SEM and TGA. X-ray diffraction (XRD) studies were conducted by means of an X'Pert PRO X-ray diffractometer (PanAnalytical, the Netherlands) operating with Cu Kα radiation (wavelength of 1.5406 Å) at 45 kV and 40 mA. The FTIR of the samples was recorded on a Perkin-Elmer Spectrum 100 spectrometer (USA) using the KBr pellet method in the spectral range 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. The morphology of the samples was studied via scanning electron microscopy (SEM, JEOL-JSM 7500F, Japan). Changes in the thermal properties of the polymer matrix after the incorporation of the clinoptilolite were studied by using

Table 1
Physicochemical characteristics of mine effluents. Q12

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

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