



Molecular simulation of geometrically optimized polyoxymethylene/poly (vinylalcohol) gel membrane for electroless scrubbing Ni(II) ions



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ABSTRACT

Perilous nickel ions are purged by polyoxymethylene/poly(vinylalcohol) (POM/PVA) gel membrane, miscibility parameters of which were optimised by computer-aided Accelrys Materials Studio that simulate compatibility of POM/PVA blending. Electroless scrubbing of Ni(II) ions was analysed economically by experimentally assessing the effects of pH, initial ion concentration, temperature and contact time which showed superior 95% adsorption and maximum adsorption capacity 475 mg/g after 7 days of optimum adsorption compared to 21.2% and 42.4 mg/g on unmodified POM thin film at neutral pH proving favouritism for membrane. Characterisation using FT-IR spectrum analysis and FESEM surface morphology advocated immense increment in adsorption efficiency. Adsorption study insinuated that Temkin's isotherm model and pseudo second order kinetic model best fit the adsorption process, while thermodynamic studies revealed spontaneity of adsorbing Ni(II) ions which were 90% recovered by 0.2 M HNO₃ in 30 min saturation time.

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1. Introduction

The presence of non-biodegradable heavy metals like nickel ions in the environment which perpetually havoc sentient lives by bioaccumulation in the food chain when exceeds the permissible limit of 0.02 mg/L in drinking water, detrimentally causes anemia, diarrhea, headache, dizziness, lung and kidney damage, shortness of breath, and central nervous system dysfunction [1–3]. To reduce the level of metal ions in wastewater has become mandatory because of the increment in chemical and industrial based agrarian activities without stringent control on the quality of effluent that contaminate environment [39]. Rinse water ousted by electroplating industries, waste water discharge from leather tanning industries and waste electrolyte from commercial electrochemical batteries are the chief sources of nickel contamination [45,46].

Adsorption has proved to be surplus for removal of metal ions from water over the affluent techniques like chemical precipitation, electrolytic extraction, electro dialysis, cementation and reverse osmosis, as these methods are inept to remove metal ions at low concentration [2]. Adsorption is a non-toxic process beneficial than photochemical treatments used for detoxification and degradation of toxic compounds which include the risk of

formation of more toxic oxidation products than the parent compounds [49]. Thus, for stamping out nickel ions, most widely used cost effective and electroless adsorption process with minimum secondary waste and scope for regeneration of adsorbent and recovery of nickel ions is employed [5,6].

POM was modified with PVA to upsurge adsorption capacity as in similar case where TiO₂ nanofibers were modified with carbon to improve efficiency of photocatalysis [52]. Many fabrication methods have been employed for removal of heavy metal ions including nanofibrous core/conjugated polymer-sheath composite in which aniline polymerise in presence of oxidant on the surface of TiO₂ forming coaxial nanocable structure or fabrication of TiO₂ nanocomposites coated with Ag nanoparticles which involve ultrasonication of dispersed TiO₂ nanofibers in silver salt solution following reduction by sodium citrate salt [47,48,50]. Amino functionalised mesoporous silica has also been used as adsorbent for adsorption of heavy metal toxic ions [51]. Although “metal like” polyoxymethylene (POM) is dormant polymer, the gelation of thermoplastic POM with poly(vinylalcohol) (PVA) in the solution mixture of *N,N*-dimethylformamide (DMF) and glycerol (1:1) was scrutinized by Accelrys Materials studio optimizing miscibility of polymers using Fluory Huggins model [4]. Chi parameter and energy of mixing were calculated to inspect compatibility and suitable blending temperature. 95% of Ni(II) ions were adsorbed on the surface of membrane which proved POM/PVA gel membrane to be advantageous over earlier reported adsorbents like sunflower

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biomass, protonated yeast or granular activated carbon with respect to sorption capacity [22,39]. Adsorption of Ni(II) ions on membrane sorbent analysed with different physical conditions appraising two parameters (Langmuir, Temkin, Freundlich, Flory Huggins, Dubinin–Radushkevich and Halsey) and three parameters (Redlich–Peterson, Sips) isotherm models along with kinetics and thermodynamics to comprehend adsorption mechanism.

2. Experiment

2.1. Materials

Polyoxymethylene (POM), poly(vinylalcohol) (PVA) [M_w = 125000], *N,N*-dimethylformamide (DMF) (99%), glycerol (99%), nickel(II) chloride hexahydrate [NiCl₂·6H₂O] (99.3% metal basis), acetic acid (99.7%), hydrochloric acid (37%), nitric acid (70%), sulphuric acid, formic acid (99%), silica gel for coating petri dish and arsenazo(III) as colouring agent for UV–vis spectrophotometry obtained from Sigma–Aldrich, India were used as received without any purification. Deionized water used for the experiment was obtained from Milipore Milli-Q system.

2.2. Apparatus

FESEM (Carl-Zeiss, Germany) to study the surface morphology, UV–vis spectrophotometer (PerkinElmer, Lambda 35, U.S.A) for quantitative appraisal, Fourier transform infrared (FT-IR) spectroscopy confirming functional bonding and Hot air oven (META-LAB Scientific, India) to accomplish solvent casting purpose were employed. Digital pH meter was used for gauging pH of the solution and screw gauge for measuring thickness of gel membrane.

2.3. Methods

POM/PVA gel membrane contains optimized 0.5% wt POM forming solid precipitate for surplus concentration was magnetic stirred at 140 °C in 20 ml solution of DMF and glycerol (1:1) and 2.5% wt PVA enough to give appropriate viscosity so that the solution could be wrought to gelatine membrane at room temperature in silica gel coated petri dish. 1000 mg/L of 500 ml nickel chloride stock solution was prepared and desired concentration required for adsorption analysis was achieved by adding apposite amount of deionized water. Adsorption kinetic studies were done assuming 35 h equilibrium time and data values for adsorbed Ni(II) ions were noted for every 5 h of time interval while optimized 95% Ni(II) ions were scrubbed for 7 days of exposure. Adsorbed Ni(II) ions for different initial concentration of Nickel Chloride solution were noted down from UV–vis spectrophotometer to plot isotherms. Thermodynamic analysis was done by adsorbing Ni(II) ions onto the membrane at variable temperature from 25 to 40 °C.

3. Results and discussion

3.1. Fabrication of POM/PVA membrane

The miscibility of POM and PVA simulated by Accelrys Materials Studio using Flory–Huggins model which has been extended to binary system of polymers inferred that Chi miscibility parameter (χ) for blending at 140 °C was lowest indicating optimum degree of miscibility. The polymers were constructed by the build module followed by geometric optimization by Forcite module using Dreiding forcefield charging for lowest energy configuration [7]. Compatibility and miscibility simulations carried out using Blends Module with 20 iterations at different temperatures were found

best at 140 °C. The Blend Module interlinking molecular simulations and modified Flory–Huggins model was used calculate binding energy between interacting POM and PVA in accordance with coordination number which evaluate the number of POM units screening PVA template molecule. For blend to be miscible the Chi parameter (χ) obtained in simulation must be less than χ_c which is calculated by [9]:

$$\chi_c = \frac{1}{2} \left(\sqrt{\frac{1}{N_a}} + \sqrt{\frac{1}{N_b}} \right)$$

Here N_a and N_b are the number of monomer units in PVA and POM respectively. Similar trend is deduced from mixing energy (E_{mix}) which decreases with increase in temperature showing lowest value of 0.492 kcal/mol at 120 °C, positive value representing the separation tendency of polymers therefore energy has to be administered for blending [10]. The mixing energy E_{mix} and the interaction parameter χ at different temperatures are listed in Table 1. which explained selectivity of POM/PVA blending [20]. The binding energy was computed as –1.48 kcal/mol at temperature of 140 °C showing permissible enthalpy for blending [42].

POM which resist common solvents was dissolved in DMF up to 0.5% wt at 140 °C, forming solid precipitate for surplus concentration [8]. Addition of Glycerol in 1:1 proportion with DMF plasticize PVA which was added at 60 °C in 2.5% wt increasing viscosity of solution [34]. Intermolecular crosslinking between aldehyde group of POM and PVA increase viscosity and finally lead to gelation while DMF containing aldehyde group is a good solvent for PVA since intra-molecular crosslinking takes place between them forming acetal brides which was in accordance with FT-IR spectrum analysis showing peaks for etheric C—O bonding and the residual solvent DMF at room temperature was casted for moisture free membrane [33,35]. The membrane was wrought by cooling the homogeneous solution in silica gel coated petri dish to room temperature whose approximate thickness of 0.11 mm was measured using screw gauge device. The membrane was solvent casted in hot air oven at 155 °C evaporating residual DMF and moisture for complete dry membrane.

The 3D special arrangement of the POM/PVA blend with 10 polymer chains was simulated by amorphous cell module employing COMPASS forcefield. The resulting cell was cubic with lattice parameter 14.8 Å showing the possible sites of hydrogen bonding.

3.2. Characterisation Study of POM/PVA gel membrane

The Fourier transform infrared (FT-IR) spectra (Fig. 1) of native adsorbent having intense peaks between 666.90–3261.04 cm⁻¹ predominantly represents stretching of alcoholic O—H, secondary amine–NH group, acidic C—O and etheric C—O bond which shifted the peaks after adsorption depicting their involvement in Ni(II) adsorption [18]. The peak of alcoholic O—H bond shifted from 3261.04 to 3264.31 cm⁻¹ whereas peak of secondary —NH group shifted to 792.99 from 794.52 cm⁻¹ revealing contribution of these bonds in nickel ions adsorption. Also, acidic C—O bond peak shifted from 1259.56 to 1258.52 cm⁻¹ and that etheric C—O from 1031.91 to 1079.99 cm⁻¹ are involved in adsorption of Ni(II) ions.

Table 1
Variation of miscibility parameters with temperature.

PVA + POM temp (°C)	Chi value	E_{mix} (kcal/mol)
25	1.015	0.601
100	0.663	0.492
120	0.668	0.522
140	0.613	0.503

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