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# 2-Mercaptobenzothiazole impregnated cellulose prepared by ultrasonication for the effective adsorption of precious metal palladium

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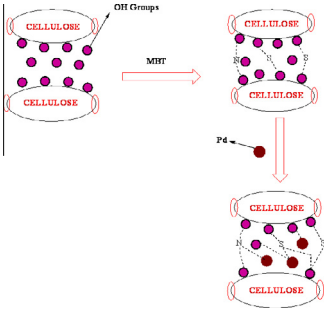
## HIGHLIGHTS

- Cellulose–Mercaptobenzothiazole adsorbent prepared by ultrasonication.
- Adsorbent used to recover palladium from a catalyst.
- The system shows adherence to D–R and Langmuir model.
- The maximum adsorption capacity of Pd(II) was 5.00 mg/g.
- The process is exothermic.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Cellulose, a natural biodegradable polysaccharide is bestowed with very good features to promote diverse applications. In this work, we report the adsorption of palladium involving its interaction with cellulose and 2-mercaptobenzothiazole. The application of FT-IR, SEM and XRD studies were used to characterize the adsorbent as well as comprehend the mechanism of the adsorption process. The ligand impregnated cellulose was prepared by ultrasonication for 20 min. The FT-IR studies showed the participation of hydroxyl functional groups in cellulose and the soft sulfur atom in mercaptobenzothiazole in the bonding between palladium and the ligand impregnated biopolymer. The stable palladium chelate is adsorbed on the surface of the ligand modified biopolymer. The concentration of palladium in the aqueous phase was measured using diphenylthiocarbazone as the complexing agent at a wavelength maximum of 584 nm. The other factors affecting adsorption such as the optimum pH, kinetics, isotherm models and thermodynamics were studied in detail. The ligand impregnated biopolymer sorbent could be regenerated using thiourea. The extraction of palladium using thiourea was confirmed from the bathochromic shift of the palladium-thiourea complex to 248 nm. As an interesting application, the mercaptobenzothiazole impregnated cellulose could be tested to recover palladium from Bis(triphenylphosphine)palladium(II)dichloride which is used in palladium catalyzed coupling reactions.



## 1. Introduction

The growing demand for noble metals in automobile industry attributed to their catalytic properties [1] has propelled the search for effective methods in their removal and recovery. The need to recover these precious metals is linked to their high cost and other environmental impacts. Palladium is one such significant metal that finds good utility as a catalyst in the production of pharmaceuticals and fine chemicals [2,3]. Chemical precipitation, ion exchange, solvent extraction, reverse osmosis and adsorption [4] are some of the well-known methods for the recovery of noble metals including palladium. The ability of palladium to function as a typical soft acid makes it appropriate to interact with sulfur containing organic ligands. The extraction of palladium (II) by sulfur-containing calix [4,6] arenes from hydrochloric acid solutions

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has been reported [5]. As a solid phase adsorbent, poly[N-(4 bromophenyl)-2-methyacrylamide-co-2-acyloamido-2-methyl-1-propanesulfonic acid-co-divinylbenzene has been reported for the removal of palladium from tap water and converter samples [6]. A solid phase extraction methodology using *Saccharomyces cerevisiae* immobilized in calcium alginate beads has been reported for the determination of Pd in road dust [7]. The sorption of palladium on hydrophobic polymers has been studied [8] using cross-linked polystyrene SSPS and 4-n-octyldiethylenetriamine. Japanese cedar wood powder was chemically modified to a tertiary-amine-type adsorbent and studied for the selective recovery of Pd(II) from diverse industrial wastes [9]. Complex gel beads comprising hydrolyzed polyacrylamide and chitosan are known for heavy metal adsorption from aqueous solutions [10]. Photoacoustic spectroscopy analysis of Pd(II)-3-[2′-thiazolylazo]-2,6-diaminopyridine complex on solid phase has also been reported [11] with an average removal efficiency of 97%. Crosslinked chitosan resin chemically modified with L-lysine has been used to examine the adsorption of Pt(IV), Pd(II), Au(III), from aqueous solutions [12]. Thiourea-HCl mixture was used to regenerate the adsorbent. Micellar-enhanced ultrafiltration with a cationic surfactant has been reported to remove palladium from water samples [13]. Mesoporous alumino silica sensors have been reported for the removal and detection of Pd(II) and Cu(II) ions [14]. Amberlite XAD-16 functionalized with 2-acetyl pyridine group has been evaluated for the solid phase extraction of palladium and other metal ions present in high level waste solution [15]. The adsorption of palladium from HCl medium has been studied using glutaraldehyde cross-linked chitosan [16]. A novel 3-(5-ethoxybenzenethiol) imino) methyl)-salicylic acid ligand immobilized onto mesoporous silica monoliths carriers shows good potential towards the recovery of palladium [17]. A novel sensor ensemble adsorbent has been investigated for rapid sensing and recovery of Pd(II) from water [18]. The adsorption of platinum and palladium using radiation cross-linked carboxymethylchitin and carboxymethylchitosan hydrogels has been reported [19]. The adsorption of Pd(II) complexes from chloride solutions obtained by leaching chlorinated spent automotive catalysts on ion exchange resin Diaion WA21J has also been investigated [20]. Sulfur containing ligands are known to bond with soft metal ions such as mercury, palladium, silver etc. Recently, mercaptobenzothiazole impregnated cellulose has shown its admirable potential toward the adsorption of mercury from aqueous solutions [21]. The success achieved in this method incited us to extend the application to palladium taking advantage of the effective soft–soft interaction of palladium with mercaptobenzothiazole. Furthermore, till date there are no literature reports involving the spectroscopic, SEM and XRD studies to understand the mechanism of interaction between palladium, cellulose and mercaptobenzothiazole. Since, cellulose is endowed with excellent properties such as biodegradability, stability, and hydrogen bonding between the polymeric chains, this polysaccharide would certainly foster good interaction with the ligand and palladium.

## 2. Experimental section

### 2.1. Reagents

Analytical grade reagents were used in all the experiments. Milli Q water (Elix 3) was used to prepare aqueous solutions of Pd(II) of varying concentrations. Cellulose was obtained from Himedia, India. Palladium (II) chloride was procured from Merck, India and 2-mercaptobenzothiazole was obtained from Sigma Aldrich. A working solution of 10 mg $L^{-1}$ Pd(II) was prepared by appropriate dilution from 1000 mg $L^{-1}$ stock Pd(II). Acetone was obtained from Himedia, India. Sulfuric acid and sodium hydroxide were procured from s.d. Fine Chemicals, India.

### 2.2. Instrumentation

The ligand mercaptobenzothiazole was impregnated onto cellulose via sonication using a Frontline sonicator (FS-500), (Frontline Electronics and Machinery, India) operating at 500 W and provided with a sound abating chamber with a diameter 36″ × 16″ × 31″ and a stainless steel tip supporting rod. The pH adjustments of the aqueous solutions were done using an Elico Li-127 pH meter supplied by Elico, India. Batch equilibration studies were conducted using an incubator shaker (Biotechnics, India). A Jasco-4200 FT-IR spectrometer was used to characterize the various functional groups in cellulose and mercaptobenzothiazole in the range 400–4000 $cm^{-1}$. A Philips PANalytical X'pert PRO diffractometer operating at 40 kV and 30 mA was utilized to record the typical changes in the diffraction pattern. The optical images were obtained using an Olympus CH20i optical microscope. A JEOL Model JSM – 6390LV and JED – 2300 were used to observe the morphological changes in the adsorbent and to record the energy dispersive X-ray spectrum (EDX) from batch studies on the adsorption of palladium. Dynamic light scattering method (DLS) using a Malvern particle size analyzer was adopted to obtain the particle size of cellulose. The concentration of palladium was measured as its dithizone complex using a Jasco V 650 UV–Visible spectrophotometer equipped with 10 mm matched quartz cells. Atomic absorption spectrophotometry (Shimadzu, AA 7000) was also used to substantiate the amount of palladium in the aqueous phase.

### 2.3. Batch adsorption study

A known (2.0 g) weight of cellulose and 25 mL of 2-mercaptobenzothiazole (0.1 mol) in acetone medium were sonicated for 20 min. The reaction mixture was filtered, washed with acetone and the solid adsorbent was dried at room temperature.

The amount of MBT impregnated onto cellulose was 0.297 g. The batch adsorption studies were carried out by equilibrating 25 mL of 10 mg $L^{-1}$ Pd(II) solution at pH 5.0 with 0.5 g of the cellulose-MBT adsorbent. The adsorption of palladium was quantified by measuring the concentration remaining in the aqueous phase using Atomic Absorption Spectrophotometry at a wavelength of 363.5 nm using an air acetylene flame. The difference between the initial Pd(II) concentration, $C_0$ and the aqueous phase concentration at equilibrium, $C_e$ was used to obtain the equilibrium amount ($q_e$) of Pd(II) adsorbed onto the cellulose-MBT adsorbent. The volume ($V$) of the aqueous phase in liters, weight ($W$) of the cellulose-MBT adsorbent in $g$, $q_e$ (amount of palladium adsorbed (mg/g) at equilibrium, $C_0$ and $C_e$ (initial and equilibrium concentrations (mg $L^{-1}$) of palladium are related as

$$q_e = (C_0 - C_e) \times \frac{v}{w} \quad (1)$$

The spectrophotometric determination of palladium in the aqueous phase was performed using dithizone as complexing agent in acidic medium. The absorbance of pink colored palladium dithizonate complex (Fig. 1) was measured at 584 nm and this confirmed the adsorption of palladium.

## 3. Results and discussion

### 3.1. Characterization

#### 3.1.1. Fourier transform infra-red (FT-IR) characterization

The FT-IR spectra (Fig. 2) of native cellulose, mercaptobenzothiazole impregnated cellulose and Pd(II)-treated adsorbent were