# Study of adsorption characteristics of Au(III) onto coal particles and their application as radiotracer in a coal gasifier

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## ARTICLE INFO

## ABSTRACT

This paper describes a systematic study carried out to investigate adsorption characteristics of $^{198}$Au onto the surface of coal particles using a radiotracer technique. The main objective of the study was to optimize labeling conditions and utilize the labeled coal particles as a radiotracer for tracing coal particles in fluidized bed coal gasifiers. The effect of various experimental factors such as pH, amount of adsorbent, initial gold concentration, temperature and contact time between adsorbate and adsorbent were studied to obtain optimum conditions for maximum adsorption of $^{198}$Au on coal particles from an aqueous solution. Analysis of the data showed that the Langmuir model was found most suitable to describe the adsorption phenomena. The thermodynamic analysis showed that the adsorption process is feasible, spontaneous and endothermic in nature. The results of the kinetics suggested that the adsorption presumably follows second order kinetics and chemisorption in nature. Based on the optimized conditions, the amount of coal particles and activity to be used for tracing the coal phase in pilot-scale gasifiers was estimated. Accordingly, the radiotracer was prepared and successfully used for measurement of residence time distribution (RTD) in a pilot-scale coal gasifier.

## 1. Introduction

Radiotracer techniques are widely used for various applications in industry and environment because of their many advantages over conventional tracers and often do not have suitable alternatives for most of the industrial situations (IAEA, 1990, 2008; Charlton, 1986; Pant et al., 2001; Jung et al., 2010). There are numerous radiotracers available for tracing liquid phases in industry that can be easily produced by irradiating suitable targets in a nuclear reactor followed by chemical processing in laboratory. In the case of tracing gas phase, enriched gaseous targets of Krypton-78 and Argon-40 are irradiated and used as radiotracers. However, for tracing solid phases in industrial systems, the radiotracers are mainly prepared using three methods i.e. direct activation, surface or volumetric labeling and artificial preparation (IAEA, 1990, 2008). None of the above-mentioned methods can be used for preparation of a radiotracer of solid phase tracing applications in all industrial situations. Different methods are used for different situations. In the direct preparation method, neutron activation analysis of the process material is performed to identify the activatable elements prior to the preparation of the radiotracer for the actual radiotracer test.

If the process material contains suitable activatable elements that can produce radioisotopes of desired nuclear characteristics, then a suitably estimated amount of the process material is irradiated in the reactor to produce the desired amount of radioactivity for use as radiotracer (Pant et al., 2001). This method is commonly used for preparation of radiotracers for tracing catalyst in Fluid Catalyst Cracking Units (FCCU) in refineries (Pant et al., 2009a), clinker rotary in cement industry and minerals (gold, copper, iron etc.) in the mineral processing industry. In surface/volumetric labeling, a suitably selected radio-isotope is labeled on the process material to prepare the radiotracer (Pant et al., 2009b, 2009c). Generally gold-198 ($^{198}$Au), scandium-46 ($^{46}$Sc), chromium-51 ($^{51}$Cr), hafnium-170/181 ($^{170/181}$Hf) radioisotopes are used to label solid matrices such as sand, silt, mud, coal, catalysts, refractory materials etc. to prepare radiotracers for tracing solid phases (IAEA, 2004). Another variant of the method is to prepare a solid phase radiotracer by adsorbing or soaking a desired radioisotope on the solid process material. In the artificial tracer method for preparation of a solid phase radiotracer, a solid material mixed with a suitable quantity of the activatable element having the identical physical properties as that of the process material is prepared and used as a radiotracer.

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Artificially prepared scandium or iridium glass particles are commonly used for preparing solid phase radiotracers in sediment transport studies (IAEA, 2014). In addition to the above three methods, mechanical tagging of the solids are also used for preparing solid phase radiotracers in radioactive particle tracking experiments and various other industrial situations (IAEA, 2004; 2014).

The adsorption approach is often used for preparation of radio-tracers for tracing coal phase in gasifiers, fluidized beds, combustors and boilers etc. in the energy industry. The approach usually involves soaking or suspending coal particles in suitably selected radioactive solution $^{198}$Au or $^{46}$Sc for a pre-decided time period followed by decanting and drying of the coal particles (Pant et al., 2009a, 2009b). Subsequently, the activity adsorbed on coal particles was estimated on the basis of comparison of initial and final concentrations of radio-activity in the radioactive and decanted solution. However, the approach provides an approximate estimation of amount of activity to be used for the tracing experiment. For estimation of an appropriate amount of activity required for tracing coal or solid phases in industrial systems, the adsorption characteristics and percentage of adsorption of the selected radioisotope is required to be known to avoid under or over estimation of activity. The use of overestimated activity will lead to saturation of the detectors and unnecessary radiation health hazards to the operators and environment. However, at the same time, the use of underestimated activity may not be sufficient for measurements. Therefore, for estimation of an appropriate amount of activity required for a radiotracer experiment, the characteristics of Au(III) should be studied and optimized conditions needed to be obtained for efficient labeling. The adsorption of any specific radioisotope on coal particles will depend on factors such as pH of the solution, concentration of the solution, temperature, soaking or stirring time, coal amount, etc. To the best of the author's knowledge, there is no study reported in the literature on adsorption characteristics of Au(III) on coal particles using the radiotracer method.

The present paper describes a systematic study carried out for the adsorption of $^{198}$Au from an aqueous solution onto the surface of coal particles with an objective to prepare radiotracer for tracing coal in gasifiers and to estimate the amount of activity to be used. The effect of experimental factors that influence the adsorption of Au(III) in form $AuCl_4^-$ of onto the coal particles, such as pH, adsorbent dose, initial gold concentration, temperature and contact time of adsorbate and adsorbent, have been assessed and a careful control has been exercised to ensure optimum adsorption using $^{198}AuCl_4^-$ as a radiotracer. Furthermore, kinetics of the adsorption and applicability of various isotherm models was analyzed. A few test runs were carried out to measure residence time distribution (RTD) of coal particles using prepared $^{198}$Au-labeled radiotracer.

## 2. Experimental

The experimental procedure involved characterization of coal particles, production and preparation of a radioactive solution of $^{198}$Au, performing the batch experiments for adsorption of coal particles and conducting a few test runs for RTD measurements. These steps are described below in detail.

### 2.1. Characterization of coal particles

The coal particles obtained from Bharat Heavy Electricals Limited (BHEL), Hyderabad India were characterized and subsequently used for adsorption studies. Bulk and true densities were determined by using specific gravity bottle and pycnometer (Thermo scientific, Mumbai, India). A sieve analysis was done using a set of IS sieves to assess the particle size distribution. Sieve analysis tests were conducted with hand shaking. Elemental analysis of coal particle was performed using a Euro Vector CHNS element analyzer (Euro EA 3000, Milan, Italy). For CHNS (Carbon, Hydrogen, Nitrogen and Sulfur) determination, samples are weighed in tin capsules and introduced into the combustion reactor where with the proper amount of oxygen and combustion catalysts, the sample is combusted. After combustion the resulting gases are carried by a helium flow, swept through a GC column to separate combustion gases and finally detected by a thermal conductivity detector (TCD). The infrared (IR) spectra were recorded using an attenuated total reflectance ATR FTIR spectrophotometer (Shimadzu IR affinity 1). The ATR accessory is equipped with a single-reflection diamond ATR hemisphere and a spring-loaded mechanical press for compacting solid samples at the ATR waveguide surface with uniform and reproducible pressure. Surface areas of coal particle samples were determined by nitrogen adsorption (BET method based on $N_2$ adsorption-desorption isotherms) using a Quantasorb adsorption unit (Quantachrome GmbH & Co. KG, Odelzhausen, Germany). The nitrogen adsorption-desorption data were recorded at liquid nitrogen temperature (77 K) and surface area was calculated using the BET (Brunauer, Emmett and Teller) equation from selected $N_2$ adsorption data. The Scanning electron microscope CamScan-4DV (CamScan, Cambridge, UK) was used to investigate surface morphology. For SEM measurements, the samples were coated with a thin layer of gold and mounted on a copper slab using a double stick carbon tape. The chemical analysis for the trace level of metal ions was carried out using Inductively Coupled Plasma-Atomic Emission Spectroscopy (Activa S ICP-OES Spectrometer, Horiba Group, UK). A high resolution γ-ray spectrometer consisting of a HPGe detector coupled to a PC-based 4 K channel analyzer (MCA) obtained from Eurysis Measures, France and analyzing software was used for γ-ray spectroscopic measurement of the $^{198}$Au sample to ascertain its radionuclide purity.

### 2.2. Production of $^{198}$Au and preparation of stock solution

Gold wire weighing 25 mg was accurately weighed, encapsulated in a quartz ampoule, kept in a cold-pressure-weld type cylindrical 1 S aluminum container [22 mm (φ) × 44 mm (l)], sealed by cold press welding and irradiated in the DHRUVA research reactor at Trombay, Mumbai in a neutron flux of $\sim 7.5 \times 10^{13}$ n cm$^{-2}$ s$^{-1}$ for one week. At the end of irradiation, the irradiated targets were cooled for 24 h, loaded in a lead shielded flask and transported from the reactor to a radiochemical processing laboratory. The irradiation container containing neutron irradiated gold wire was taken in a lead shielded container to radioisotope processing facility, the seal of the irradiation container was cut opened with the help of an opening unit and the irradiated target was transferred to a 150 mL three necked round bottom flask. About 10 mL aqua regia solution (3:1 M ratio of HCl to HNO$_3$) was added slowly through the funnel and heated gently at 100 °C to dissolve the gold wire till a yellowish solution was obtained. The solution was heated until near dryness to expel nitric acid. The residue was then reconstituted in 10 mL of 0.1 N HCl and heated to near dryness; this step was repeated three times. Finally, H$^{198}$AuCl$_4$ as solution was filtered through a G2 filter assembly and collected in a vial connected serially. After appropriate dilution and sampling, the radionuclide purity of the samples was assessed using a pre-calibrated high resolution HPGe detector system coupled to a multi-channel analyzer (MCA). A pre-calibrated ionization chamber (Beta-Gamma standard type 1383A, General Radiological Ltd, England) was used for the measurement of radioactivity content of $^{198}$Au. Activity content of the $^{198}$Au solution used for adsorption studies were determined by a 3" x 3" well type NaI(Tl) scintillation counter (Para Electronics India Pvt. Ltd, Mumbai, India).

A stock solution of HAuCl$_{4(aq)}$ of concentration 1000 mg L$^{-1}$ was prepared by adding a weighed amount of the HAuCl$_4$ (1 g) to 1000 mL of de-ionized water. The stock solution was spiked with 37 MBq (1 mCi) of $^{198}$Au as H$^{198}$AuCl$_4$. This stock solution was subsequently diluted by water of appropriate volume to prepare HAuCl$_4$ solution of different concentrations as per experimental requirement.