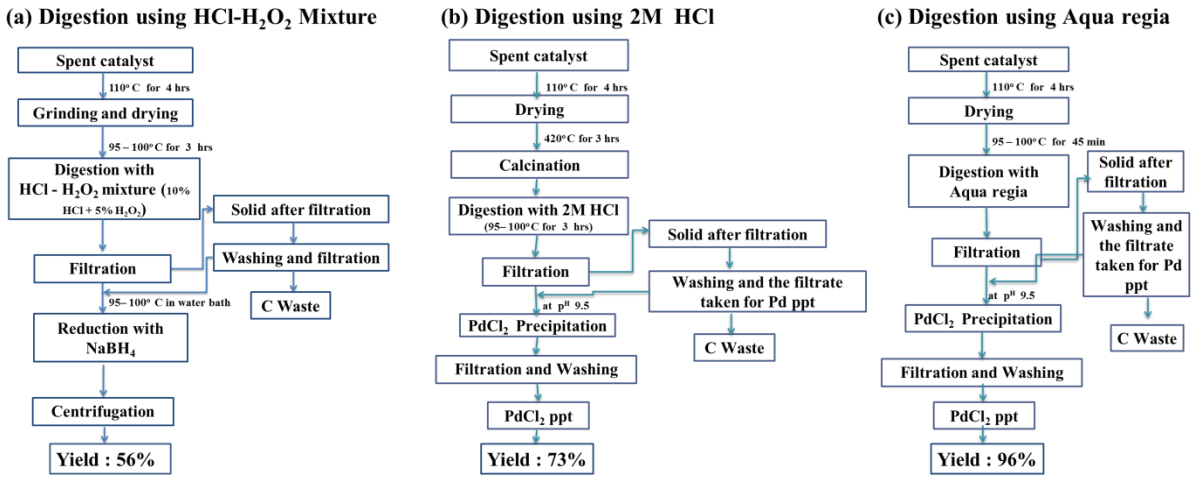
Supplementary Information

SI 1. Catechin and polyphenol profile of green tea (Ref: *Generally Recognized As Safe Status Of Green Tea Catechin, Kao Corporation, Food and Drug Administration, 2007*)

Component	% composition
Total catechin monomer	44.4
Polyphenols	52.9
Caffein	2.6
Relative catechin profile (% of Total catechin monomers)	
Catechin (C)	2.0
Epicatechin (EP)	6.8
Gallocatechin (GC)	5.4
Epigallocatechin (EGC)	29.8
Catechingallate (CG)	1.0
Epicatechin gallate (ECG)	10.4
Gallocatechingallate (GCG)	1.1
Epigallocatechingallate (EGCG)	43.7



SI 2. Palladium (Pd) extraction protocols for Pd/C followed in the present work. Three different routes for extraction of Pd were chosen for the study *viz*. digestion using (a) HCl-H_2O_2, (b) 2M HCl and (c) Aqua regia.

SI 2(a). Extraction Procedure

Method 1

The spent catalyst (Pd/C) was ground and sieved through 75 µm sieve. The finely powdered spent catalyst was dried at 110 ± 5 ˚C for 4 hrs. About 1g of the dried finely powdered spent catalyst was digested with 20 mL of 10% HCl – 5% H_2O_2 mixture for about 3 hrs at 95-100 ˚C under magnetic stirrer and filtered. The digestion was repeated two more times at the same temperature for half an hour to ensure the complete extraction. The extract was then used for the precipitation of Pd using $NaBH_4$ as the reducing agent.

Method 2

The spent catalyst (Pd/C) was dried in an electric oven at 110 ± 5 ˚C for 4 hrs. About 1g of the dried sample was calcined at 420-450 ˚C for 4 hrs. It was then digested with 20 mL of 2M HCl for 4 hrs at 95-100 ˚C under magnetic stirrer and filtered. The extraction was repeated twice to ensure the complete extraction of Pd from Pd/C. The extract was then used for the precipitation of Pd by adjusting the pH using NaOH.

Method 3

The spent catalyst (Pd/C) was dried at 110 ± 5 ˚C for 4 hrs. About 1g of the dried sample was digested with 5 mL of aqua regia for about 45 min. 5 mL of distilled water was added to it and was refluxed for another 20 min. The hot solution was filtered through Whatman 42 filter paper. 5 mL of aqua regia solution was added again and the solution was refluxed for 30 minutes. 5 mL of distilled water was added to it and the solution was boiled for 20 minutes. The solution was filtered through Whatman 42 and the filtrate was collected in the same standard flask. The operation was repeated thrice to ensure the complete removal of Pd from Pd/C.

125 mL of the filtrate was evaporated to dryness; the residue was dissolved in minimum quantity of 20% HCl, and the evaporation process was repeated. This process was continued thrice to ensure complete removal of nitrate ion to avoid interference later during the Pd precipitation step. Finally, the residue was dissolved in minimum quantity of 20% HCl and diluted to 100 mL followed by precipitation of Pd by adjusting the pH using NaOH.

SI 2(b). Pd recovery %: Calculation steps for AAS analysis

The spent Pd impregnated carbon used for the present work contains 6.5% of Pd. *i.e.* 1 g of spent catalyst contains 65 mg of Pd. To carry out AAS analysis, the acid/acid mixture extracted solution was made up to 250 mL. The working sample was prepared by taking 250 μL of the extract and made up to 5 mL. The calibration standards for the analysis were prepared by using the NIIST traceable standards provided by Thermo scientific. The detailed calculation is given below.

Method 1: HCl-H_2O_2 Method

Sample 1

Weight of sample taken for the analysis = 1.0070g

∴ Expected amount of Pd present in 1.0070g sample = (65x1.0070)/1

= 65.455mg

If 100% recovery is there, then the concentration of the extract should be 261.82 ppm.

From AAS,

Concentration of working sample = 7.6814 ppm

∴ Concentration of the extract = 7.6814 x 20

= 153.63 ppm

⇒ In mg, 38.4075* mg of Pd is present in 250 mL of the extract

* (65.455 x 153.63) / 261.82 = 38.4075 mg

∴ % recovery of Pd by HCl-H_2O_2 method = (153.63/261.82) x 100

= 58.68%

For the precipitation of Pd, 125 mL of the extract was used. *i.e.*, it contains 19.2038 mg of Pd. The precipitated Pd, after drying was dissolved in minimum quantity of aqua regia and made up to 100 mL. So the concentration of the solution is 192.038 ppm. 500 μL of the made up solution is further diluted to 10 mL and is used as the working sample for AAS analysis.

From AAS,

Concentration of the working sample = 9.1565 ppm

∴ Concentration of the sample = 9.1565 x 20

= 183.13 ppm

⇒ (183.13/192.038) x 100 =95.36 % of Pd is precipitated.

⇒ In terms of mg, 36.63 mg of Pd is precipitated

∴ The absolute recovery of Pd = (36.63/65.455) x 100

= 55.96 %

Sample 2

Weight of sample taken for the analysis = 1.0027 g

∴ Expected amount of Pd present in 1.0070g sample = (65x1.0027)/1

= 65.1755 mg

If 100% recovery is there, then the concentration of the extract should be 260.702 ppm.

From AAS,

Concentration of working sample = 7.7014 ppm

∴ Concentration of the extract = 7.7014 x 20

= 154.028 ppm

⇒ In mg, 38.507* mg of Pd is present in 250 mL of the extract

* (65.1755 x 154.028) / 260.702 = 38.507 mg

∴ % recovery of Pd by HCl-H_2O_2 method = (154.028/260.702) x 100

= 59.09%

For the precipitation of Pd, 125 mL of the extract was used. *i.e.*, it contains 19.2535 mg of Pd. The precipitated Pd, after drying, was dissolved in minimum quantity of aqua regia and made up to 100 mL. So the concentration of the solution is 192.535 ppm. 500 μL of the made up solution is further diluted to 10 mL and is used as the working sample for AAS analysis.

From AAS,

Concentration of the working sample = 9.2549 ppm

∴ Concentration of the sample = 9.2549 x 20

= 185.1 ppm

⇒ (185.1/192.535) x 100 =96.14 %of Pd is precipitated

⇒ (38.507x96.14)/100 = 37.02 mg can be precipitated from the extract

∴ Absolute recovery of Pd = (37.02/65.1755) x 100

= 56.80%

Method 2: 2M HCl Method

Sample 1

Weight of sample taken for the analysis = 1.0046 g

∴ Expected amount of Pd present in 1.0070g sample = (65x1.0046)/1

= 65.299 mg

If 100% recovery is there, then the concentration of the extract should be 261.196 ppm.

From AAS,

Concentration of working sample = 9.7955 ppm

∴ Concentration of the extract = 9.7955 x 20

= 195.91 ppm

⇒ In mg, 48.9775* mg of Pd is present in 250 mL of the extract

* (65.299 x 195.91) / 261.196 = 48.9775 mg

∴ % recovery of Pd by 2M HCl method = (195.91/261.196) x 100

= 75.01%

For the precipitation of Pd, 125 mL of the extract was used. *i.e.*, it contains 24.4888 mg of Pd. The precipitated Pd, after drying, was dissolved in minimum quantity of aqua regia and made up to 100 mL. So the concentration of the solution is 244.888 ppm. 200 μL of the made up solution is further diluted to 10 mL and is used as the working sample for AAS analysis.

From AAS,

Concentration of the working sample = 4.8088 ppm

∴ Concentration of the sample = 4.8088 x 50

= 240.44 ppm

⇒ (240.44/244.888) x 100 =98.18 %of Pd is precipitated

⇒ (48.9775 x 98.18)/100 = 48.09 mg can be precipitated from the extract

∴ Absolute recovery of Pd = (48.09/65.299) x 100

= 73.65%

Sample 2

Weight of sample taken for the analysis = 1.0022 g

∴ Expected amount of Pd present in 1.0070g sample = (65x1.0022)/1

= 65.143 mg

If 100% recovery is there, then the concentration of the extract should be 260.572 ppm.

From AAS,

Concentration of working sample = 9.5842 ppm

∴ Concentration of the extract = 9.5842 x 20

= 191.684 ppm

⇒ In mg, 47.921* mg of Pd is present in 250 mL of the extract

* (65.143 x 191.684) / 260.572 = 47.921 mg

∴ % recovery of Pd by 2M HCl method = (191.684/260.572) x 100

= 73.56%

For the precipitation of Pd, 80 mL of the extract was used, *i.e.*, it contains (47.921x80)/250= 15.3347 mg of Pd. The precipitated Pd, after drying, was dissolved in minimum quantity of aqua regia and made up to 100 mL. So the concentration of the solution is 153.347 ppm. 500 μL of the made up solution is further diluted to 10 mL and is used as the working sample for AAS analysis.

From AAS,

Concentration of the working sample = 7.5784 ppm

∴ Concentration of the sample = 7.5784 x 20

= 151.568 ppm

⇒ (151.568/153.347) x 100 =98.84 %of Pd is precipitated

⇒ (47.921 x 98.84)/100 = 47.37 mg can be precipitated from the extract

∴ Absolute recovery of Pd = (47.37/65.143) x 100

= 72.72%

Method 3: Aqua regia Method

Sample 1

Weight of sample taken for the analysis = 1.0033 g

∴ Expected amount of Pd present in 1.0070g sample = (65x1.0033)/1

= 65.2145 mg

If 100% recovery is there, then the concentration of the extract should be 260.858 ppm.

From AAS,

Concentration of working sample = 12.2544 ppm

∴ Concentration of the extract = 12.2544 x 20

= 245.088 ppm

⇒ In mg, 61.272* mg of Pd is present in 250 mL of the extract

* (65.2145 x 245.088) / 260.858 = 61.272 mg

∴ % recovery of Pd by aqua regia method = (245.088/260.858) x 100

= 93.95%

For the precipitation of Pd, 125 mL of the extract was used. *i.e.*, it contains 30.636 mg of Pd. The precipitated Pd, after drying, was dissolved in minimum quantity of aqua regia and made up to 100 mL. So the concentration of the solution is 306.36 ppm. 400 μL of the made up solution is further diluted to 10 mL and is used as the working sample for AAS analysis.

From AAS,

Concentration of the working sample = 12.2402 ppm

∴ Concentration of the sample = 12.2402 x 25

= 306.01 ppm

⇒ (306.01/306.36) x 100 =99.89 %of Pd is precipitated

⇒ (61.272 x 99.89)/100 = 61.20 mg can be precipitated from the extract

∴ Absolute recovery of Pd = (61.20/65.2145) x 100

= 93.84%

Sample 2

Weight of sample taken for the analysis = 1.0025 g

∴ Expected amount of Pd present in 1.0070g sample = (65x1.0025)/1

= 65.1625 mg

If 100% recovery is there, then the concentration of the extract should be 260.65 ppm.

From AAS,

Concentration of working sample = 12.8672 ppm

$\therefore$ Concentration of the extract = 12.8672 x 20

= 257.344 ppm

$\Rightarrow$ In mg, 64.336* mg of Pd is present in 250 mL of the extract

* (65.1625 x 257.344) / 260.65 = 64.336 mg

$\therefore$ % recovery of Pd by Aqua regia method = (257.344/260.65) x 100

= 98.73%

For the precipitation of Pd, 50 mL of the extract was used. *i.e.*, it contains 12.8672 mg of Pd. The precipitated Pd, after drying, was dissolved in 15 mL of aqua regia and made up to 100 mL. So the concentration of the solution is 128.672 ppm. 500 μL of the made up solution is further diluted to 10 mL and is used as the working sample for AAS analysis.

From AAS,

Concentration of the working sample = 6.5692 ppm

$\therefore$ Concentration of the sample = 6.5692 x 20

= 131.384 ppm

$\Rightarrow$ (131.384/128.672) x 100 =102.1 %of Pd is precipitated (The high value may be attributed to the error in volume)

$\Rightarrow$ (64.336x100)/100 = 64.336 mg can be precipitated from the extract

$\therefore$ Absolute recovery of Pd = (64.336/65.1625) x100

= 98.73 %

SI 2(c). A tentative economic comparison of the three methods employed in our study for the extraction of Pd from 1 kg of spent Pd/C

1.	Percentage of Pd metal present in the used catalyst (%)	6.5		
2.	Quantity of Pd present in 1 kg of spent catalyst, *i.e.* Pd/C (g)	65.00		
3.	The quantity of Pd that can be recovered (g) in this study	HCl-H_2O_2 method	2M HCl method	Aqua regia method
		36.64	47.59	62.59

Economic comparison of the three methods used for the Pd extraction used in this study*

Parameter considered	**Method 1 (HCl-H_2O_2 extraction)**		**Method 2 (2M HCl extraction)**		**Method 3 (Aqua regia extraction)**	
Materials (Chemicals)	Chemicals used	HCl,H_2O_2 & $NaBH_4$	Chemicals used	HCl & NaOH	Chemicals used	HCl, HNO_3 & NaOH
	Approx. Cost (In INR)	15,805/-	Approx. Cost (In INR)	3664/-	Approx. Cost (In INR)	12,869/-
	Remark	✓	Remark	✓	Remark	✓
Process (In hours)	Duration	4 Hrs	Duration	9 Hrs	Duration	5 Hrs
	Remark	✓	Remark	✓	Remark	✓
Pd recovery	Recovery %	~ 56	Recovery %	~ 73	Recovery %	~ 96
	Additional $PdCl_2$ required to make up 6.5% (g)	28.36	Additional $PdCl_2$ required to make up 6.5% (g)	17.41	Additional $PdCl_2$ required to make up 6.5% (g)	2.41
	Approx. Cost (in INR)	1,12,362/-	Approx. Cost (in INR)	69,075/-	Approx. Cost (in INR)	9550/-
	Remarks	✗	Remarks	✗	Remarks	✓

***** The numbers in the table are purely based on the cost of the purchased chemicals and the time taken for the extraction processes in our lab. The rate of Palladium is based on Sigma Aldrich price catalog.