FUJI SILYSIA CHEMICAL

CHROMATOREX

Technical Bulletin

SILICA GEL

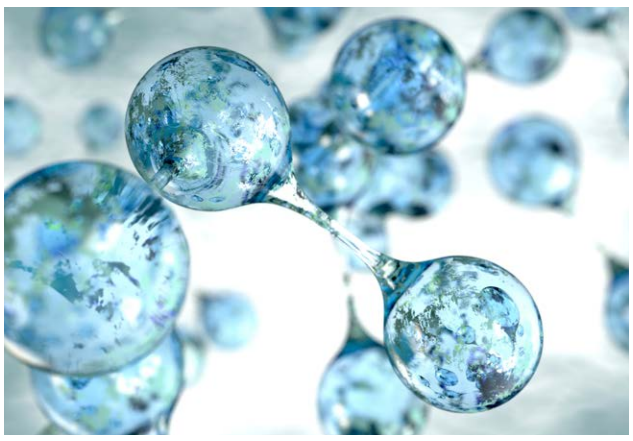
For Metal Scavenger

INTRODUCTION

Silica for removing heavy metals (scavenger)

In recent years, organic synthesis methods using transition metal catalysts have been applied in many applications, such as the Suzuki-Miyaura reaction. At the same time of the study of this synthesis method, the removal of used metals from the reaction system was a major issue. After these processes, removing the residual heavy metals is just as important as the development of catalyst reaction process. One of the removal methods is to introduce a functional group that specifically binds metal to the solid surface and use it as a scavenger. However, if the first objective of the transitional metal removal is to get an API with high purity and feasible economy, a second objective is to improve the environmental sustainability with waste recycling and/or potential precious metal recovery, key factors in the pharmaceutical industry. We manufacture metal scavengers with various functional groups on silica gel that has a large surface area (porous material), and has high strength and solvent resistance. It can be used widely from research to plant level.

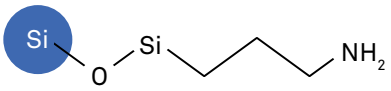
Removing the residual heavy metals is just as important as the development of catalyst reaction process.



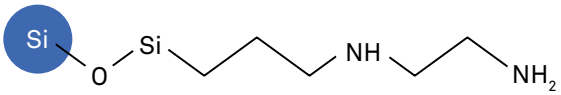
GRADES

Our silica grades with 4 functional groups are:

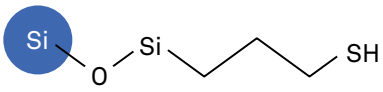
NH Silica



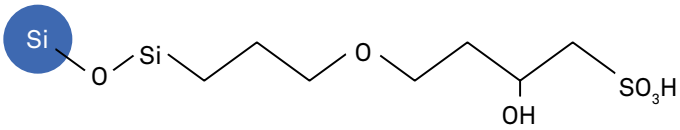
Diamine Silica



SH Silica



SO_3H Silica



BASE SILICA PROPERTIES

The base silica gel is spherical and suitable for column and batch processing operations.

Shape	Spherical
Average particle size	100 μm
Average pore diameter	SO_3H : 7 nm (70 Å) NH, Diamine, SH : 10 nm (100 Å)

GRADE AND ADSORPTION SPECIES

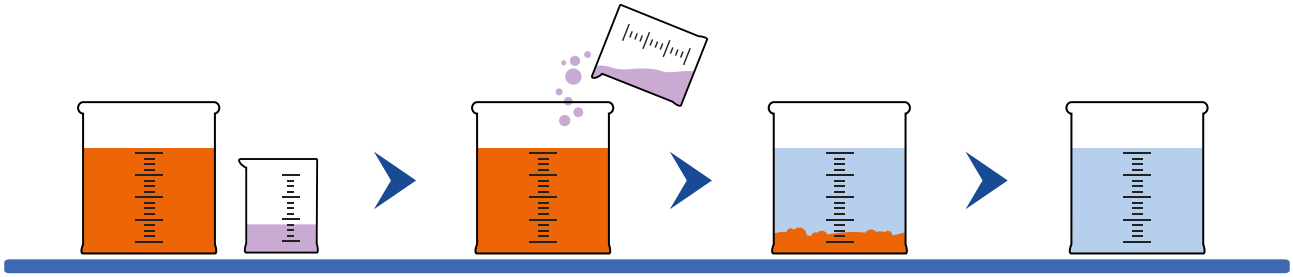
The following table shows the targeted adsorbate species that each metal scavenger grade removes. Please select according to the application.

Grade	Adsorption species
NH Silica	Ni, Cu, Pd
Diamine Silica	Ni, Cu, Zn, Ru, Pd, Cd, Pb
SH Silica	Ru, Pd, Pt, Hg
SO_3H Silica	Fe, Co, Ru

PROCESSING OPERATION METHOD

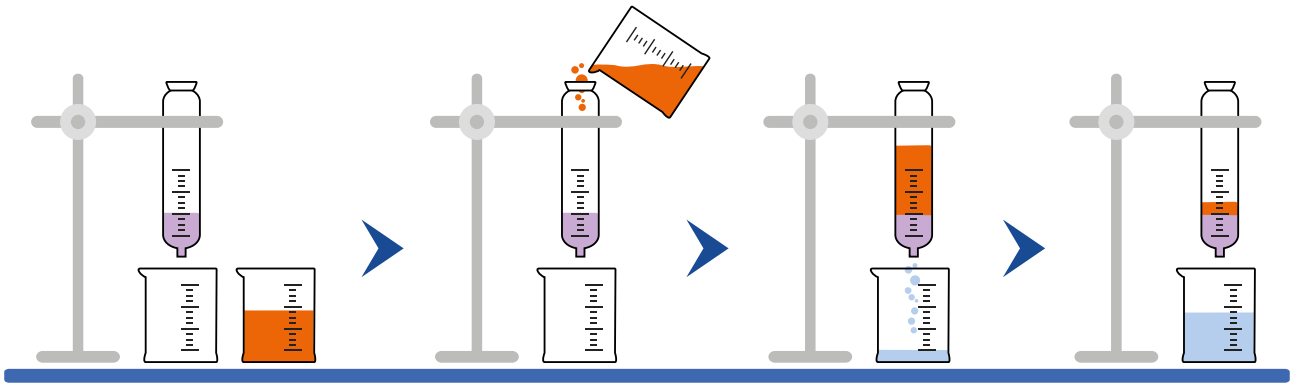
Heavy metal can be removed by adding scavenger silica for metal removal to a metal solution by either batch type or column type.

BATCH



Heavy metals can be removed by adding scavenger silica to the solution containing heavy metals, stirring for a certain period of time and filtering.

COLUMN



Prepare a column packed with scavenger silica and remove heavy metals by flowing down a solution containing heavy metals.

ADSORPTION OF VARIOUS METALS

Various “silica for heavy metal removal” were added to the metal solution, and the amount of metal adsorbed after the adsorption treatment was measured.

MEASURING METHOD

Metal solution (25 mL, containing 5 mg of metal) + Silica for heavy metal removal (125 mg or 250 mg or 625 mg) → Stir at room temperature 30 min → Filtration → Evaporation to dryness → Prepare in aqueous solution → Atomic absorption analysis or ICP emission spectroscopy

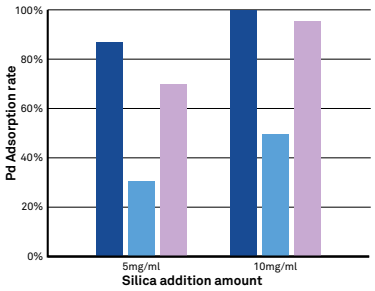
SH Silica　NH Silica　Diamine Silica　SO_3H Silica

Pd (0) SH Silica and Diamine Silica are recommended.

Pd (II) SH Silica, NH Silica, Diamine Silica: All showed good adsorption.

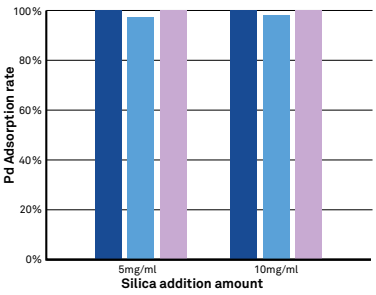
Pd (0)

$Pd(dba)_2/CHCl_3$ solution (Pd 200 mg/L)



Pd (II)

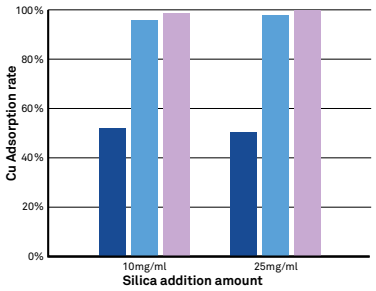
$Pd(OAc)_2/CHCl_3$ solution (Pd 200 mg/L)



Cu (I),**Cu (II)** NH Silica and Diamine: Shows good adsorption.
NH Silica is recommended.

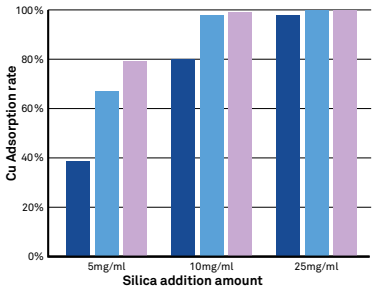
Cu (I)

CuCl/DMF solution (Cu 100 mg/L)



Cu (II)

$Cu(OAc)_2$/MeCN solution (Cu 200 mg/L)

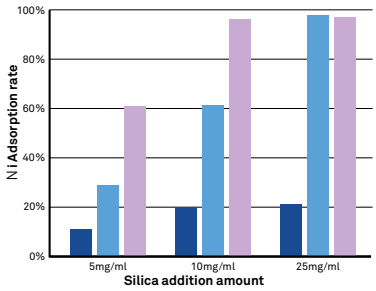


Ni (II) NH Silica and Diamine Silica: Showed good adsorption.
NH Silica and Diamine Silica are recommended.

Fe (III) SO_3H Silica: Showed good adsorption.
SO_3H Silica is recommended.

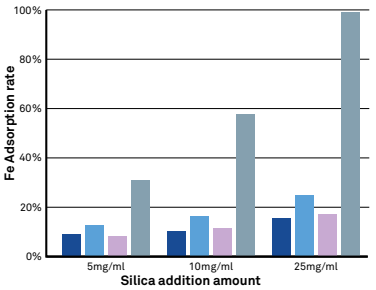
Ni (II)

Ni(acac)/THF solution (Ni 200 mg/L)



Fe (III)

$Fe(acac)_3$/MeCN solution (Fe 200 mg/L)



EFFECT OF SOLVENT

Prepared Pd solution for each solvent 25 mL of 200 mg/L (Pd as 5 mg contains) 250 mg of Silica for heavy metal removal. The Pd removal ability when added and stirred for 30 minutes at room temperature was evaluated. Adsorption performance varies depending on the combination of ligand, solvent, and surface functional group. Use different types of silica for heavy metal removal depending on the sample conditions.

EXCLUSION RATE

Adsorption species	Pd (II) / Pd $(OAc)_2$			Pd (0) / Pd $(dba)_2$		
Solvent	$CHCl_3$	THF	Toluene	$CHCl_3$	THF	Toluene
Diamine Silica	>97.5%			>85.0%	>97.5%	
NH Silica	>85.0%			<85.0%	>85.0%	
SH Silica	>97.5%			>97.5%		

ADSORPTION CAPACITY

The table shows the adsorption capacity of each grade for each solvent (the amount of metal removed per gram of silica for heavy metal removal). The adsorption capacity in the table was calculated based on the amount of metal adsorbed when 100 mg of silica for heavy metal removal was added to a 20 mL of 200 mg / L metal solution (containing 4 mg of metal).

	Adsorption capacity (mmol/g)								
Adsorption species	Pd (II) / $Pd(OAc)_2$			Pd (0) / $Pd(dba)_2$			Ni (II) / $Ni(acac)_2$		
Solvent	$CHCl_3$	THF	Toluene	$CHCl_3$	THF	Toluene	THF	DMF	DMSO
Diamine Silica	0.64	0.82	0.74	0.18	0.27	0.31	0.41	0.41	0.61
NH Silica	0.42	0.63	0.55	0.09	0.21	0.15	0.24	0.10	0.08
SH Silica	0.60	0.74	0.64	0.23	0.27	0.31	0.09	0.06	0.04

Since Pd (II) has a large adsorption capacity, it was tested under the condition of a metal solution volume of 50 mL

	Adsorption capacity (mmol/g)								
Adsorption species	Cu (II) / $Cu(OAc)_2$			Cu (I) / CuCl			Fe (III) / $Fe(acac)_3$		
Solvent	MeCN	THF	DMF	DMF	DMSO	–	MeCN	THF	Toluene
Diamine Silica	0.50	0.51	0.40	0.15	0.13	–	0.05	0.03	0.03
NH Silica	0.41	0.47	0.35	0.15	0.15	–	0.08	0.02	0.09
SH Silica	0.24	0.24	0.19	0.05	0.10	–	0.06	0.04	0.09
SO_3H Silica	–	–	–	–	–	–	0.19	0.18	0.20

Since Cu (I) has low solubility in CuCl, the concentration of the metal solution should be 100 mg / L. The test was conducted accordingly.

ADSORPTION REMOVAL SPEED

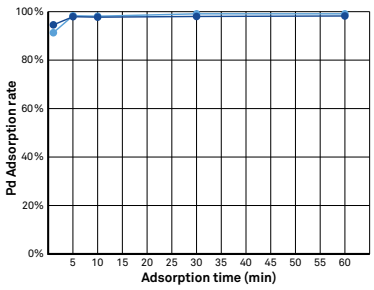
20 mL of Pd solution 200 mg / L and 20 mL of Ni solution 100 mg / L were prepared as samples for the adsorption removal rate measurement, then 200 mg of heavy metal removal silica was added to each solution while stirring. The time-dependent changes in Pd and Ni adsorption rates at room temperature after addition were measured by atomic absorption spectrometry.

Pd Adsorption removal rate

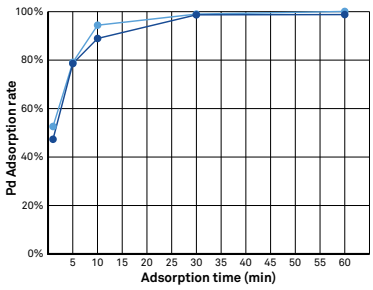
The Pd (II) adsorption reached equilibrium within 10 minutes after adding Silica, and the Pd (0) adsorption reached equilibrium in about 30 minutes.

SH Silica NH Silica

Pd (II) / Pd (OAc)$_2$



Pd (0) / Pd (dba)$_2$

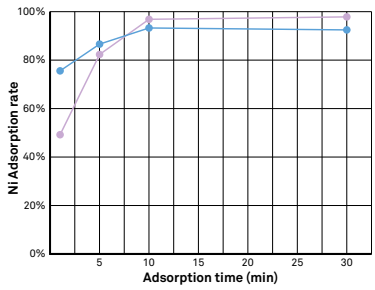


Ni Adsorption removal rate

Silica is added into Ni (II) solution and the adsorption of Ni reached equilibrium in about 10 minutes.

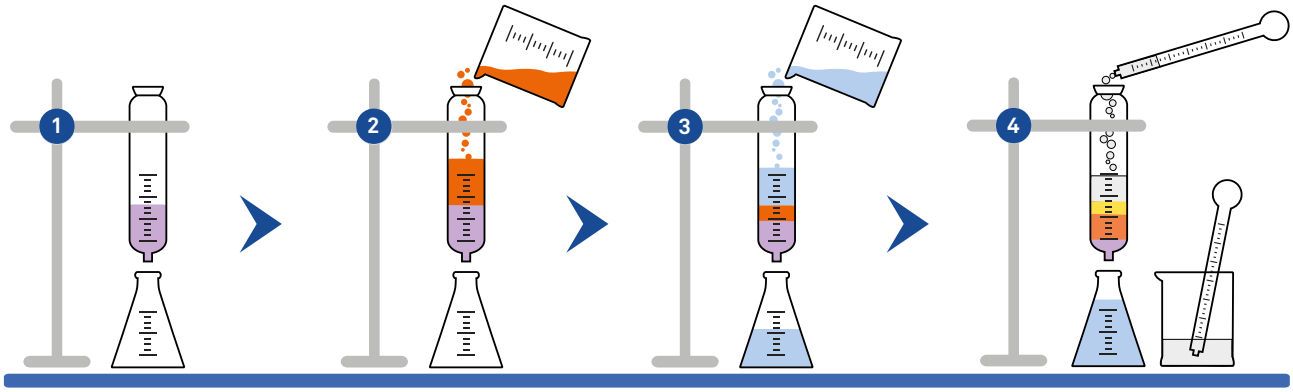
NH Silica Diamine Silica

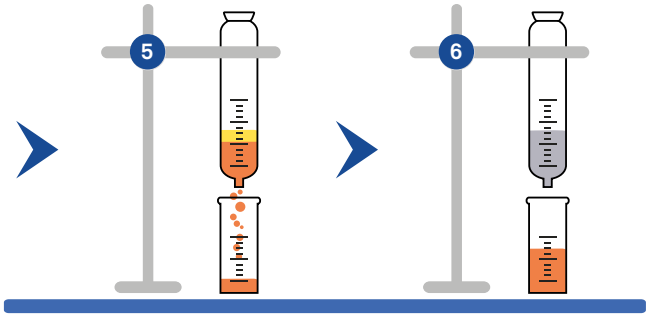
Ni (II) / Ni (acac)$_2$



ADSORPTION AND DESORPTION

An example of Pd adsorption and desorption recovery using Diamine Silica cartridge is shown. More than 95% of Pd can be recovered.





Desorption solvent:
2% thiourea / 1 M HCl / MeOH solution.

1. Set the column with Diamine Silica
2. Flow down the Pd solution
3. Wash the column with solvent
4. Add desorption solvent
5. Collect the eluted Pd
6. Complete elution and finish

SH Silica has strong adsorption force with Pd and does not elute under these conditions.

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