Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1185744

57 (2016) 29352–29362
December

Taylor & Francis
Taylor & Francis Group

Functionalized mesoporous silica: absorbents for water purification

Saima Nasreen[a,b,c,*], Afshan Urooj[b], Uzaira Rafique[b], Sheryl Ehrman[c]

[a]*Department of Environmental Sciences, International Islamic University, Islamabad, Pakistan, email: saima_mq@yahoo.com (S. Nasreen)*
[b]*Department of Environmental Sciences, Fatima Jinnah Women University, The Mall, Rawalpindi 46000, Pakistan, emails: afshan_urooj@hotmail.com (A. Urooj), uzairaiqbal@yahoo.com (U. Rafique)*
[c]*Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742, USA, email: sehrman@umd.edu (S. Ehrman)*

Received 14 December 2015; Accepted 10 April 2016

ABSTRACT

The release of heavy metals into the environment is a potential threat to water and soil quality as well as to plants, animals, and human health. In the current research work, organically functionalized mesoporous silicates (MSU-H) were prepared by the co-condensation between sodium silicate and organoalkoxysilanes in the presence of the nonionic surfactant triblock copolymer P104. The surfactant was used as a template for improving the porosity of hybrid gels. Synthesized materials were characterized. The surface morphology and textural properties of such materials varied with various kinds of groups in the channels. In this study, removal of some heavy metal ions from aqueous solution by adsorption process was investigated. Batch adsorption studies show that the adsorption capacity of metal ions on the functionalized silicates is more than that on pure MSU-H. Data show adsorption on synthesized materials is a time-efficient process, suggesting adsorption on external surface as well as the mesoporous process. Adsorption models of Langmuir, Freundlich, and Temkin depicted equal goodness for all adsorbents, whereas pseudo-second-order kinetics is in best agreement with experimental data.

Keywords: Silica hybrids; Porous materials; Metal ions; Adsorption; Equilibrium; Kinetics

---

1. Introduction

Mesoporous silica materials have received great attention due to diverse and useful applications ranging from adsorbents for contaminants and as catalysts support. Natural environment has been a subject of various effects of chemicals emitted during anthropogenic as well as natural processes. The accumulation of these activities is generating global environmental changes. Moreover, population boost and technological advancements have challenged environmental safety [1,2]. Therefore, recognition of pollutants and prevention of their environmental dispersions are one of the necessities in this field, and consequently pollution prevention methods must be specified. Treatment technologies emerged to decrease the harmful effect on the

---

*Corresponding author.

Presented at the 8th International Conference on Challenges in Environmental Science & Engineering (CESE-2015) 28 September–2 October 2015, Sydney, Australia

environment and the industrial discharge without negative consequences. Wastewater treatment technologies have strong future perspectives.

Mesoporous materials during the last decade have been widely explored for applications in environmental remediation. Novel families of porous solids having fascinating regular mesostructure, high specific surface areas, thermal, and mechanical stability, high adsorption capacity, and wide possibilities of functionalization [3–20] were testified.

Silica-based organic–inorganic hybrid [21–24] and, more recently, ordered Mesoporous organosilica materials developed as adsorbents for sequestering pollutants such as heavy metal ions, metalloids, inorganic anions, phenolic compounds, polyaromatic hydrocarbons, pesticides, and dyes from water samples [8,19,25–28]. However, for such environmental applications, Mesoporous silica materials do not exhibit specific binding sites. Accordingly, immobilization of suitable functional groups in the mesopores [10,29] is carried out by either using a functionalized silane, co-condensing a silane with silica source, or post modification of Mesoporous silica.

Metals are problematic environmental pollutants, with well-known toxic effects on living systems [30]. Metals cannot be degraded or destroyed [31]. To a small extent they enter our bodies via food, drinking water, and air. Their presence in compartments of environment is posing threats. The discharge from industries ending up into the water bodies is adversely affecting the life of humans as well as aquatic organisms. Some metals such as lead and mercury easily cross the placenta and damage the brain [32]. Scientists are faced with a number of challenges directly related to metal pollution.

Organic–inorganic hybrids represent an important class of synthetic engineering materials. The combination of properties of individual components and development of new properties on hybridization opened a fast expanding area of research having diverse applications [33–36]. These Hybrids have progressively found their place as economical adsorbents with significant synthetic advances and technological development.

Metals such as Cu, Cd, Pb, Hg, Ni, Co, and Zn are introduced into the environment as a result of natural process of weathering and erosion of rocks. These and few other metals are added to the ecosystems through wastewater polluted by industrial process such as chemical manufacturing, metal finishing, tannery, and use of fertilizers, and pesticides [37].

The identification of metals in different environmental compartments is a great challenge. Ground water sources are continuously being contaminated by the release of toxic pollutants. The most disastrous threat is posed by mercury, arsenic, lead, and chromium.

Mercury is a known and potential human carcinogen and neuro poison. They refused and discarded consumer products like fluorescent light bulbs, electrical fixtures, auto switches, thermostats, and medical equipment releases mercury to the environment. The organic and inorganic ligands make strong complexes, making mercury soluble in oxidized aquatic systems.

The chemistry of arsenic is complex due to its presence in several oxidation states. Arsenic compounds are used to make special glass, semi-conductors, dyes, and drugs. Seafood and drinking water also contain arsenic. Many arsenic compounds sorb strongly to soils and are therefore transported in groundwater and surface water.

Lead and lead containing compounds are very toxic for human health and the environment. It causes inhibition of some enzymes activity and disruption in the nervous system resulting in severe health problems, ending up by death. Beside that it causes lower IQs, behavioral changes, and concentration disorder in children [38,39]. Lead is listed as No. 2 out of 783 hazardous substances Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40].

Chromium is widely used in industrial applications as corrosion inhibitor [41] in cooling towers, metal plating, leather tanning, and dye manufacture [42]. Chromium can be found in the natural environment, however, large doses of Cr(VI) are linked to cancer, skin ulcers, and other maladies [43]. Evidence of human health impacts have also been shown in several DNA interaction studies with chromium [44–46]. The removal of metal ions from wastewaters is a much needed subject for research. Different approaches and methods are attempted by scientists, but most of these processes are unacceptable, owing to the disposal of sludge, their high cost, low efficiency, and inapplicability to a wide range of pollutants [47].

The functionalized silica hybrids are synthesized in the present work to explore the opportunities for optimal route and factors (choice of precursor and surfactant) affecting the structure-activity properties and adsorption efficiency. In the present investigation, the Synthesized Mesoporous Silica hybrid materials are applied in batch experiment to assess the feasibility of these materials as adsorbents for the remediation of toxic metals.

2. Material and methods

This research is an attempt to synthesize functionalized MSU-H hybrids with P104 as non-ionic structure directing agent and sodium silicate as silica precursor with five different organosilanes with organic moieties of 3-Aminopropyltrimethoxysilane (APTMS); 3-Glucidoxypropyltrimethoxysilane (GPTMS); 3-Methacryloxypropyltrimethoxysilane (MPTMS); Vinyltrimethoxysilane (VTMS); and Phenyltrimethoxysilane (PTMS). Synthesized MSU-H functionalized materials as adsorbents are applied for the removal of selected metal ions and other compounds like phenols reported elsewhere [48].

2.1. Synthesis of MSU-H

MSU-H was synthesized using 7.26 g of P104, 300 mL of water and 30 mL of acetic acid. The mixture was stirred at room temperature for 1 h, followed by drop-wise addition of 8.84 mL of sodium silicate solution. The solution was aged at 60℃ for 20 h, filtered, and washed with water. The solid product was oven dried and calcined at 600℃ for 4 h [49].

2.2. Synthesis of functionalized silica hybrids

Synthesized Mesoporous silica (MSU-H) was subjected to functionalization with organosilanes having five different organic moieties. Direct co-condensation method was opted.

For the functionalization of MSU-H, sodium silicate solution was applied as precursor. The direct co-condensation synthesis procedure follows addition of surfactant (4.0 g of P104) and 8 g KCl in 100 mL of water and 15 mL of Acetic acid at room temperature. A known amount of precursor was added and pre-hydrolyzed for 2 h. Organosilane (1.08 g) with a known organic moiety (APTMS) was added to the mixture under stirring (20 h) at 60℃ and static conditions of heating (at 100℃ for 24 h) for functionalization. The material was collected by filtration, dried in air, and extracted with ethanol. Excessive Pluronic was washed with ethanol to remove template, filtered, and dried under vacuum at 100℃ for 3 h [50].

The same procedure was repeated for organosilanes with organic moieties of GPTMS; MPTMS; VTMS; and PTMS.

Five functionalized Mesoporous silica of MSU-H were coded as AM, GM, MM, VM, PM representing different organic moieties.

2.3. Characterization of functionalized silica hybrids

Each of the synthesized material was comprehensively characterized by a wide range of techniques to determine the surface and bulk characteristics [48].

2.4. Adsorption protocol

Adsorbent dose with known mass (3 mg) of each MSU-H Functionalized hybrid is added to a known initial concentration (100 ppb) of metal (mercury, arsenic, lead, chromium) salt solution at neutral pH. The contact of hybrid (adsorbent) and metal (adsorbate) is made for a known time (20 min) on the shaker (Lab-companion SK-300). An aliquot is drawn after every 2 min, filtered, and analyzed on Inductively Coupled Plasma Spectrophotometer with Mass Spectrometer (ICP-MS) (7500, Single Turbo System, Agilent) to determine the remaining concentration in the solution. The adsorbed concentration on the adsorbent or uptake on each hybrid is calculated by Eq. (1):

$$q_{\mathrm{e}} = \left(\frac{C_{\mathrm{i}} - C_{\mathrm{e}}}{W}\right) V \tag{1}$$

where C_{i}, C_t, and C_{e} (mg/L) are the liquid-phase concentrations of adsorbate initially, at time t and at equilibrium, respectively. V is the volume (L) of the solution and W is the weight (g/L) of sorbent.

Removal of Metals (%R) by the synthesized functionalized silica hybrids is determined from the relation given in Eq. (2):

$$\%R = \left(\frac{C_{\mathrm{i}} - C_t}{C_{\mathrm{i}}}\right) 100 \tag{2}$$

2.5. Equilibrium and kinetic studies

The equilibrium data obtained in the present investigation as a result of batch adsorption experiments are treated with well-known adsorption isotherms and kinetic equations.

The conformity between experimental data and adsorption model or adsorption kinetics predicted values is expressed by the correlation coefficient (R^2 values close or equal to 1). A relatively high R^2 value indicates that the model successfully describes the kinetics of adsorption [51].

3. Results and discussion

Each of the synthesized material was subjected to standardized characterization techniques and then applied as adsorbents for metal ions remediation form wastewater.

3.1. Synthesis and characterization of silica hybrids

It is evident that Mesoporous silica MSU-H is prepared from sodium silicate solution. It is noted that selection of precursor is an important parameter for tailoring the structures in successful synthesis. A wide range of possibilities in using low-cost and convenient reagents are reported in the literature. The present study results indicated sodium silicate as a relatively better precursor than conventionally used TEOS and TMOS. This is manifested by the smaller particle size and increased surface area of MSU-H (see Table 1). A similar influence on the pore characteristics is observed by [52–55]. It might be attributed to the fact that small size of sodium silicate cannot be too large for steric hindrance [54]. On the contrary, larger species of TMOS containing more Si–O–Si bonds results in larger pore size.

Another preference is demonstrated by higher hydrothermal and thermal stability of product by using sodium silicate. The reason for the improvement of the structural order and hydrothermal stability is that the silica precursor consisting of the larger species induces better resistance against structural breakdown during calcination and hydrothermal treatment. Thermal and hydrothermal stability for Mesoporous silica prepared from fumed silica is reported by other researchers [52,53].

The functionalized silica hybrids are synthesized by direct co-condensation of five different organosilanes with sodium silicate solution. It is noted that success of this method rests on the compatibility of organo-alkoxysilane precursor with the synthesis conditions.

The present results revealed good compatibility of selected organic silanes with the synthesis conditions. This is manifested by negligible chemical or structural damage. It is evident from Table 1 that hexagonal geometry of Mesoporous Silica is distorted to tetragonal and orthorhombic upon functionalization. It is also concluded that this route provides an easy and homogeneous distribution [56–58] of organic moiety in the functionalized silica hybrids. Further, this method also facilitates a drop in porosity and reaction time upon functionalization in comparison to grafting method.

The purpose of functionalization is to increase the adsorption efficiency through incorporation of the organic linkages/bonding and thus providing more pore volume and surface area to the incoming pollutants.

The preference of functionalization through organic moiety is to keep intact the basic framework of silica and moreover the development of inorganic to organic linkages broaden the application window of the prepared/synthesized adsorbents. The presence of both organic and inorganic elements/groups in the same framework makes it a good adsorbent for the cumulative removal of organic and inorganic pollutants from the mixed environment of wastewater comprising of diverse pollutants.

Each of the functionalized silica hybrids applied as adsorbents for the removal of chromium, lead, mercury, and arsenic from the aqueous media in a batch protocol. The uptake of each metal was analyzed on ICP-MS.

Table 1
Description of functionalized mesoporous silica hybrids

Sample code	Details	XRD symmetry	Pore volume	Surface area	particle size
MSU-H	Na_2SiO_3 precursor with P104 as structure directing agent	Hexagonal	0.0689	580.27	10.34 nm
AM	Functionalized MSU-H with 3-aminopropyltrimethoxysilane (APTMS)	Orthorhombic	−0.0047	44.28	135.48 nm
GM	Functionalized MSU-H with 3-glucidoxypropyltrimethoxysilane (GPTMS)	Tetragonal	−0.0009	4.77	1.25 μm
MM	Functionalized MSU-H with 3-methacryloxypropyltrimethoxysilane (MPTMS)	Tetragonal	−0.0097	86.08	69.69 nm
VM	Functionalized MSU-H with vinyltrimethoxysilane (VTMS)	Orthorhombic	−0.0056	36.86	162.75 nm
PM	Functionalized MSU-H with phenyltrimethoxysilane (PTMS)	Orthorhombic	−0.0105	114.47	52.41 nm

3.2. Adsorption application for metals decontamination

Each of the functionalized silica hybrids with five different organic moieties reveals interesting adsorption trends for the uptake of metals. The graphical presentations (see Fig. 1) show striking unanimously adhered decreasing adsorption sequence of Pb ≥ Cr > As > Hg.

On further probe, it appears that GM and PM have almost superimposed adsorption for Pb and Cr with significantly lower removal percentage of Hg by the earlier than later. On the contrary, a regular incremental increase from mercury to chromium is demonstrated by AM, VM, and MM. It is also noted that effect of organic moiety is manifested on the percentage removal. The minimum and maximum adsorption for the metals depicts range of 62–96%, 38–99%, 68–99%, 79–93%, and 67–98% on AM, GM, MM, VM, and PM, respectively.

The contribution of functionalization in the adsorptive removal of metals is also considered. Improved adsorption capacity for metals is also attributed to functionalization [59,60].

The cumulative efficacy of silica based adsorbents and metal uptake is exhibited largely in Fig. 2(a) and (b). This interdependence of an adsorbent and metal ion is found consistent through the whole spectrum of analysis. The efficacy scale of adsorbents follows the sequence:

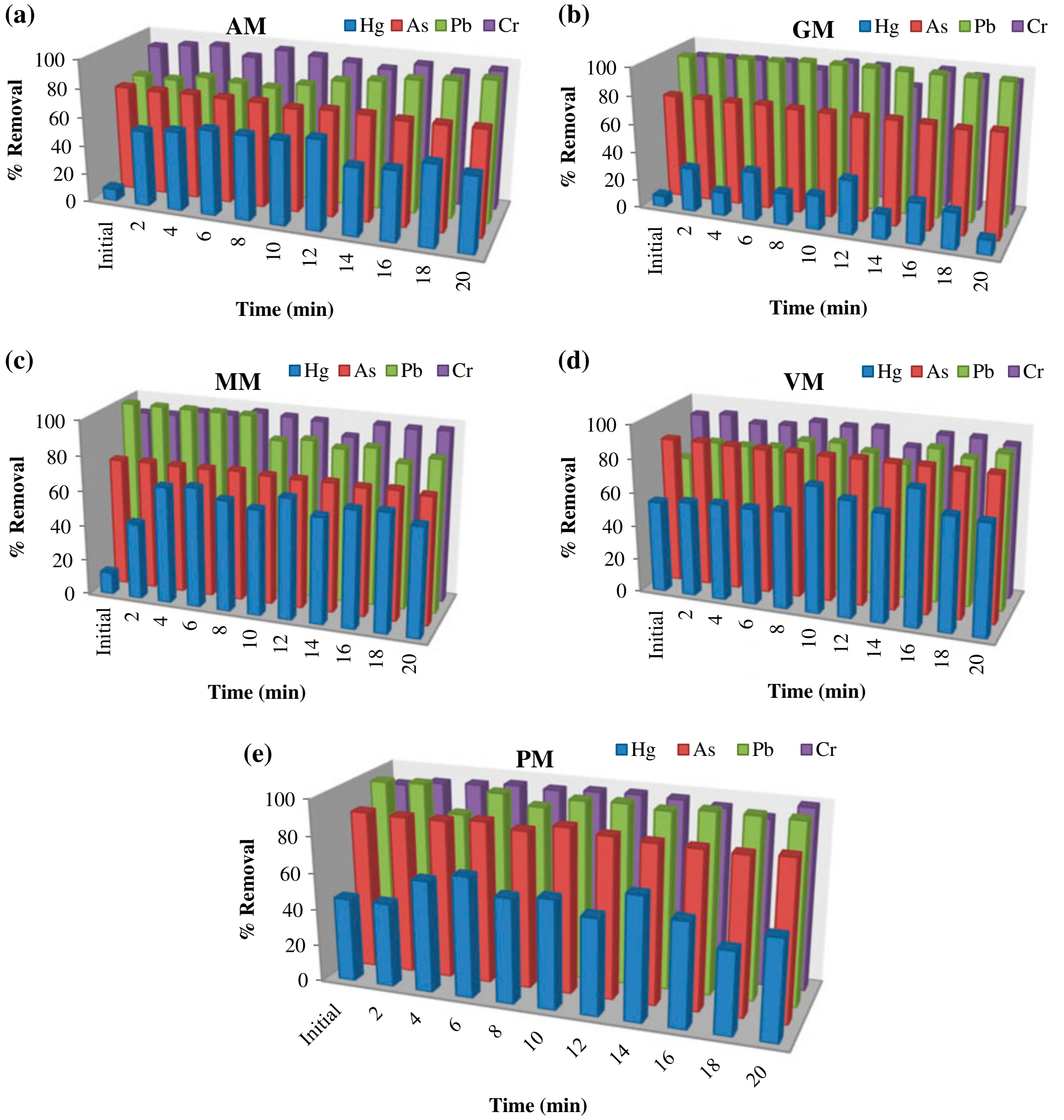

Fig. 1. Removal (% age) of metal ions on functionalized silica hybrids (a) AM, (b) GM, (c) MM, (d) VM, and (e) PM.

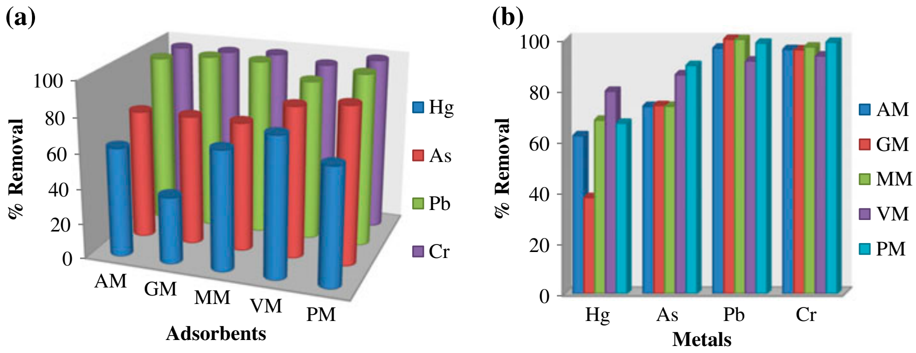

Fig. 2. Adsorption trends (%*R*) as a function of (a) functionalized hybrids and (b) metal ions.

VM > MM > PM > AM > GM (for Hg)
PM > VM > GM > MM > AM (for As)
GM > MM > PM > AM > VM (for Pb)
PM > MM > GM > AM > VM (for Cr)

The qualitative performance scale of each adsorbent is characterized as Excellent for Chromium, Very good for Lead, Good for Arsenic and fairly good for Mercury. The adsorption capacity and rate of adsorption of Cr by functionalized silica also found excellent by Li, 2008 [61]. However, average adsorption efficiency of Chromium on all the adsorbents is more than any other metal ion whereas the two adsorbents GM and MM, individually remove more lead in comparison to Chromium (Fig. 3).

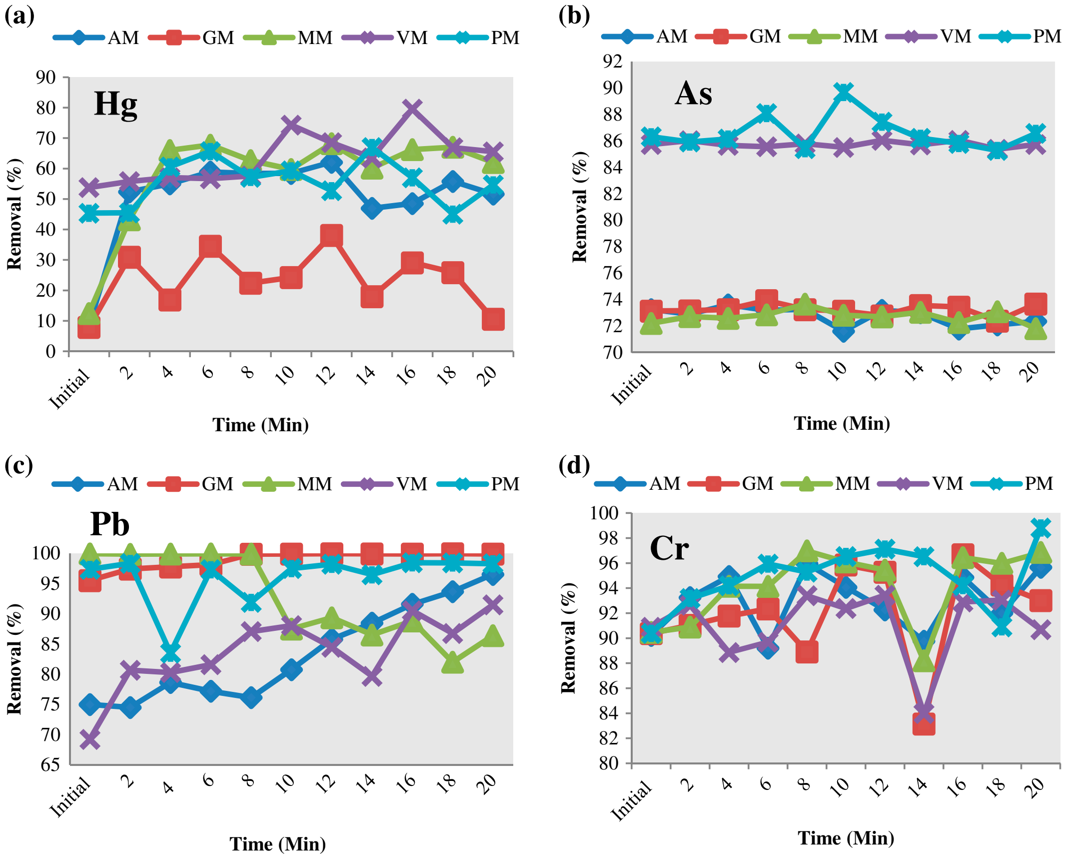

Fig. 3. Metals adsorption trends as a function of contact time (a) Hg, (b) As, (c) Pb and (d) Cr.

Table 2
Langmuir, Freundlich, and Temkin isotherms analysis against sorption variables for metal ions

Sorbents	SBA-15	MSU-H	VO	PO	AM	GM	MM	VM	PM
Langmuir parameters: mercury									
q_m (mg/g)	35.46	40.81	42.37	5.34	4.977	3.409	8.968	42.19	29.41
K_L (L/mg)	−0.065	−0.079	0.088	−0.029	−0.024	−0.016	−0.031	−0.089	0.050
R^2	0.988	0.991	0.983	0.739	0.93	0.818	0.904	0.988	0.985
Lead									
q_m (mg/g)	5.524	5.015	4.72	3.157	7.142	9.615	8.510	6.443	8.278
K_L (L/mg)	−1.56	−1.26	−1.72	−0.534	−5.76	−115	−97.5	−3.001	−28.09
R^2	0.996	0.985	0.995	0.988	0.996	0.999	0.998	0.990	0.998
Arsenic									
q_m (mg/g)	51.28	54.64	70.42	72.99	52.63	53.47	52.91	73.5	76.33
K_L (L/mg)	−0.123	−0.148	−0.39	−0.46	−0.13	−0.13	−0.134	−0.492	−0.639
R^2	0.999	0.999	1	1	1	0.999	0.999	1	0.999
Chromium									
q_m (mg/g)	98.03	92.59	75.75	88.49	85.47	80.64	86.20	79.3	88.49
K_L (L/mg)	−145.7	−21.6	−0.862	−3.531	−2.017	−1.22	−2.416	−0.906	−3.89
R^2	1	0.999	0.997	0.999	0.999	0.997	0.999	0.998	0.999
Freundlich parameters: mercury									
n	−1.56	−1.858	−2.049	−0.621	−0.433	−0.265	−5.076	−2.040	−1.253
K_F (mg/g)	2.237	2.372	2.449	1.583	1.344	1.080	19.69	2.449	2.063
R^2	0.982	0.982	0.965	0.774	0.916	0.921	0.738	0.969	0.98
Lead									
n	−3.012	−2.732	−2.865	−1.328	−7.246	−125	−5.076	−4.950	−16.12
K_F (mg/g)	461.6	145.05	−84.12	11.16	−37.21	−126.7	19.69	−53.66	−42.2
R^2	0.985	0.95	0.96	0.986	0.925	0.88	0.738	0.933	0.902
Arsenic									
n	−2.525	−2.857	−5.241	−5.847	−2.645	−2.724	−5.076	−6.016	−7.042
K_F (mg/g)	2.592	2.676	3.000	3.043	2.625	2.645	19.69	3.054	3.109
R^2	0.999	0.998	0.999	0.999	0.999	0.999	0.738	0.999	0.996
Chromium									
n	−250	−88.49	−8.620	−21.69	−13.45	−5.076	−15.15	−8.849	−23.25
K_F (mg/g)	3.336	3.343	3.184	3.305	3.254	19.69	3.272	3.175	3.310
R^2	0.677	0.544	0.936	0.885	0.98	0.916	0.966	0.974	0.883
Temkin parameters: mercury									
B (kJ/mol)	−38.56	−34.62	−32.21	−50.69	−61.57	−76.21	−53.74	−32.27	−43.78
K_T (L/g)	0.005	0.004	0.003	0.008	0.009	0.009	0.008	0.003	0.006
R^2	0.993	0.992	0.984	0.965	0.984	0.996	0.981	0.985	0.993
Lead									
B (kJ/mol)	−2.482	−2.62	−2.438	−4.263	−1.18	−0.078	−0.263	−1.646	−0.572
K_T (L/g)	0.019	0.023	0.022	0.061	0.0006	3.03E-54	3.65E-15	0.004	1.81E-07
R^2	0.991	0.973	0.972	0.995	0.939	0.884	0.949	0.955	0.912
Arsenic									
B (kJ/mol)	−28.402	−25.93	−16.02	−14.63	−27.43	−26.84	−27.28	−14.25	−12.45

(*Continued*)

Table 2 (*Continued*)

Sorbents	SBA-15	MSU-H	VO	PO	AM	GM	MM	VM	PM
K_T (L/g)	0.002	0.002	0.0003	0.0002	0.002	0.002	0.002	0.0001	7.15E-05
R^2	0.999	0.999	1	0.999	0.999	0.999	0.999	0.999	0.997
Chromium									
B (kJ/mol)	−0.398	−1.095	−10.17	−4.359	−6.886	−7.851	−6.217	−10.12	−4.135
K_T (L/g)	1.8E-10	1.2E-39	1.7E-05	7.5E-11	2.0E-07	1.1E-06	5.0E-08	1.4E-05	2.4E-11
R^2	0.68	0.55	0.948	0.894	0.983	0.93	0.97	0.979	0.891

The 3D view of the scale is shown in Fig. 2(b). The theoretical understanding gives an insight into the preference for the metal uptake. The highest uptake of active Cr is attributed to its transition nature that imparts catalytically immobilized [62–64] behavior on adsorbents.

3.3. Equilibrium and kinetic study

Application of isotherms and kinetic models is done to explore the mode of adsorption for metal ions onto functionalized silica-based hybrid surfaces.

3.3.1. Batch sorption equilibrium dynamics

Equilibrium isotherms are applied to get an insight of sorption mechanism to propose surface properties and affinity of adsorbents. The treatment of present study data to Langmuir, Freundlich, and Temkin Isotherms demonstrated $R^2 \approx 1$ for each of the synthesized silica hybrids, applied as adsorbent for the removal of metal ions (see Table 2).

Langmuir explains the significant relationship of the amount adsorbed on the surface of synthesized adsorbents to the residual concentration of the metals in the following sequence: As > Cr > Pb > Hg (see Table 2). The good fitness of Langmuir for all the adsorbents suggests the maximum saturation of metal pollutants on the mono surface layer [65] suggesting that material is composed of multilayered components. The uptake of As onto the synthesized adsorbents suggests that mechanism is capillary diffusion through the pores in comparison to surface attachment of mercury, lead, and chromium. The quantity of the pollutant adsorbed on the surface layer is decreasing linearly. Temkin model confirm even dissemination of metal ions within the pores of adsorbent. Therefore, the quantity adsorbed on the surface layer has a linear relationship for Removal of mercury by all the adsorbents. The fitness of experimental data to Temkin parameters for the removal of metal pollutants follow the general sequence as: As > Hg > Pb > Cr.

Further, smaller value of $1/n$ and larger value of K_F indicates that the adsorbent has greater affinity for a particular metal ion over another [64]. It is interesting to note that negligibly small values of "n" are calculated for each metal adsorbed on prepared composites (see Table 2). In addition, the negative values of heat of sorption represented as B (kJ/mole) indicate weak sorbate–sorbent interaction proposing a shallow physisorption wells for pollutants uptake on the surface of composites [66].

3.3.2. Kinetic studies and adsorption capacity (q_e)

Validation of zero order, pseudo-first-order, and pseudo-second-order equations for Metal ions adsorption is explored from linear plots. Kinetic studies suggest that for designing of a good adsorbent the variable parameters, the fitness of pseudo-second-order indicate dependence of adsorption on more than one factors.

In the present study, the incorporation of different organic moieties into the silica network for functionalization provides more binding sites. Optimizations of available binding sites for adsorption are few parameters evaluated for development of good adsorbents.

Functionalized silica hybrids are applied as adsorbents for the removal of metal ions from the aqueous solution in batch protocol. The experimental data are evaluated for the adsorption capacity (q_e) of each adsorbent and pollutant removal. Based on the adsorption capacity (q_e) value for metal ions, the functionalized silica adsorbents exhibited adsorption efficiency of 311–329 mg/g. It is interesting to note that Lead follows "Good," Mercury and Arsenic exhibiting "Very Good;" whereas Chromium reveals "Excellent" adsorption on functionalized silica hybrids. The general sequence of adsorbent efficiency of silica hybrids for the Metals removal follows:

PM > MM > GM > AM > VM

4. Conclusions

(1) The synthesis of hybrids with diverse organic moieties is significant to provide opportunities to understand the role of each component in the hybrid. It also broadens the scope for application as potential adsorbents for removal of metal ions.

(2) The present study concludes the successful application of synthesized hybrids as adsorbents in batch mode for the decontamination of metal cations by showing show striking unanimously adhered decreasing adsorption sequence of Pb ≥ Cr > As > Hg.

(3) It is also noted that effect of organic moiety is manifested on the percentage removal. The minimum and maximum adsorption for the metals depicts range of 62–96%, 38–99%, 68–99%, 79–93%, and 67–98% on AM, GM, MM, VM, and PM, respectively.

(4) The qualitative performance scale of each adsorbent is characterized as excellent for chromium, very good for lead, good for arsenic and fairly good for mercury.

(5) Adsorption isotherms of metal ions are well-fitted with the Langmuir, Freundlich and Temkin Isotherms and the adsorption kinetics follows the pseudo-second-order model. The modeling confirms that the uptake is a chemisorption process.

Acknowledgements

The authors thank NISP Lab and FabLab at University of Maryland, College Park USA and Fatima Jinnah Women University, Rawalpindi Pakistan, for providing the necessary techniques for characterization of synthesized materials and their applications. Authors also gratefully acknowledge HEC (Higher Education Commission, Pakistan) for providing IRSIP fellowship to Saima Nasreen for pursuing her doctoral research at UMD, USA.

References

[1] H.R. Rahmani, M. Rezaei, Effluent of industrial effluents of Zob- Ahan on soil, water and vegetable plants, J. App. Sci. 7 (2007) 72519–72522.

[2] A.K.M.R. Rahman, S.M. Hossain, M.M. Akramuzzaman, Distribution of heavy metals in rice plant cultivated in industrial effluent receiving soil, Environ. Asia 3(2) (2010) 15–19.

[3] F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, Silica-based mesoporous organic–inorganic hybrid materials, Angew. Chem. Int. Ed. 45 (2006) 3216–3251.

[4] Y. Wan, D.Y. Zhao, On the controllable soft-templating approach to mesoporous silicates, Chem. Rev. 107 (2007) 2821–2860.

[5] C. Sanchez, C. Boissière, D. Grosso, C. Laberty, L. Nicole, Design, synthesis, and properties of inorganic and hybrid thin films having periodically organized nanoporosity, Chem. Mater. 20 (2008) 682–737.

[6] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism, Nature 359(6397) (1992) 710–712.

[7] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, A new family of mesoporous molecular sieves prepared with liquid crystal templates, J. Am. Chem. Soc. 114 (1992) 10834–10843.

[8] A. Stein, B.J. Melde, R.C. Schroden, Hybrid inorganic-organic mesoporous silicates-nanoscopic reactors coming of age, Adv. Mater. 12(19) (2000) 1403–1419.

[9] P.T. Tanev, T.J. Pinnavaia, A neutral templating route to mesoporous molecular sieves, Science 267 (1995) 865–867.

[10] A. Sayari, S. Hamoudi, Periodic mesoporous silica-based organic-inorganic nano-composite materials, Chem. Mater. 13 (2001) 3151–3168.

[11] G.J.D.A. Soler-Illia, C. Sanchez, B. Lebeau, J. Patarin, Chemical strategies to design textured materials: From microporous and mesoporous oxides to nanonetworks and hierarchical structures, Chem. Rev. 102 (2002) 4093–4138.

[12] B. Lebeau, J. Patarin, C. Sanchez, Design and properties of hierarchically organized hybrid organic-inorganic nanocomposites, Adv. Technol. Mater. Mater. Proc. 6 (2004) 298–307.

[13] J. Liu, Y. Shin, L.-Q. Wang, G.J. Exarhos, J.H. Chang, G.E. Fryxell, Z. Nie, T.S. Zemanian, W.D. Samuels, in: Nanostructured Catalysts, S.L. Scott, C.M. Crudden, C.W. Jones (Eds.), Kluwer Academic/Plenum Publishers, New York, NY, 2003, pp. 297–310.

[14] G. Kickelbick, Hybrid Inorganic–organic mesoporous materials, Angew. Chem. Int. Ed. 43 (2004) 3102–3104.

[15] A. Vinu, K.Z. Hossain, K. Ariga, Recent advances in functionalization of mesoporous silica, J. Nanosci. Nanotechnol. 5(3) (2005) 347–371.

[16] R.J.P. Corriu, A. Mehdi, C. Reyé, Molecular chemistry and nanosciences: On the way to interactive materials, J. Mater. Chem. 15 (2005) 4285–4294.

[17] B. Hatton, K. Landskron, W. Whitnall, D. Perovic, G.A. Ozin, Past, present, and future of periodic mesoporous organosilicas The PMOs, Acc. Chem. Res. 38 (2005) 305–312.

[18] G.E. Fryxell, The synthesis of functional mesoporous materials, Inorg. Chem. Commun. 9 (2006) 1141–1150.

[19] G.E. Fryxell, Y. Lin, S. Fiskum, J.C. Birnbaum, H. Wu, K. Kemner, S. Kelly, Actinide sequestration using self-assembled monolayers on mesoporous supports (SAMMS), Environ. Sci. Technol. 39 (2005) 1324–1331.

[20] B. Lebeau, F. Gaslain, C. Fernandez-Martin, F. Babonneau, Ordered Porous Solids, in: V. Valtchev, S. Mintova, M. Tsapatsis (Eds.), Elsevier Ltd., Oxford, 2009, pp. 283–308.

[21] J.F. Biernat, P. Konieczka, B.J. Tarbet, J.S. Bradshaw, R.M. Izatt, Complexing and chelating agents immobilized on silica gel and related materials and their application for sorption of inorganic species, Sep. Purif. Rev. 23 (1994) 77–348.

[22] L.L. Tavlarides, J.S. Lee, Synthesis and application of functionalized organo-ceramic selective adsorbents, Ion Exch. Solvent 14 (2001) 169–227.

[23] P.K. Jal, S. Patel, B.K. Mishra, Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions, Talanta 62 (2004) 1005–1028.

[24] H.-J. Im, T.L. Yost, Y. Yang, J.M. Bramlett, X. Yu, B.C. Fagan, L.R. Allain, T. Chen, C.E. Barnes, S. Dai, L.E. Roecker, M.J. Sepaniak, Z.-L. Xue, Organofunctional sol-gel materials for toxic metal separation, ACS Symposium Series Nuclear Waste Management, Accomplishments of the Environmental Management Science Program 943 (2006) 223–237.

[25] L. Mercier, V. Bell, in: H. Mostaghaci (Ed.), Environment Conscious Materials: Ecomaterials, Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, 2000, pp. 599–606.

[26] Y. Kim, J. Yi, Advances in environmental technologies via the application of mesoporous materials, J. Ind. Eng. Chem. 10(1) (2004) 41–51.

[27] M. Jaroniec, O. Olkhovyk, Synthesis and characterization of ordered mesoporous materials for removal of heavy metal ions, NATO Sci. Ser. II. 228 (2006) 325–336.

[28] M.C. Burleigh, S. Dai, Functionalized nanoporous adsorbents for environmental remediation, Ser. Chem. Eng. 4 (2004) 756–771.

[29] H. Yoshitake, Highly-controlled synthesis of organic layers on mesoporous silica: Their structure and application to toxic ion adsorptions, New J. Chem. 29 (2005) 1107–1117.

[30] C.R. Evanko, D.A. Dzombak, Remediation of Metals-Contaminated Soils and Groundwater, Technology Evaluation Report, 1997.

[31] S. Davydova, Heavy metals as toxicants in big cities, Microchem. J. 79 (2005) 133–136.

[32] T.R. Levine, R.K. Kim, H.S. Park, M. Hughes, Deception detection accuracy is a predictable linear function of message veracity base-rate: A formal test of Park and Levine's probability model, Commun. Monogr. 73 (2006) 243–260.

[33] W. Wang, B. Gu, L.Y. Liang, W. Hamilton, Fabrication of near infrared photonic crystals using highly monodispersed submicrometer SiO_2 spheres, J. Phys. Chem. B 107(44) (2003) 12113–12117.

[34] W. Wang, B. Gu, L.Y. Liang, W. Hamilton, Fabrication of two and three-dimensional silica nanocolloidal particle arrays, J. Phys. Chem. B 107(15) (2003) 3400–3404.

[35] W. Wang, B. Gu, Self-assembly of two- and three-dimensional particle arrays by manipulating hydrophobicity of silica nanoparticles, J. Phys. Chem. B 109(47) (2005) 22175–22180.

[36] W. Wang, B. Gu, L. Liang, Effect of anionic surfactants on synthesis and self-assembly of silica colloidal nanoparticles, J. Colloid Interface Sci. 313(1) (2007) 169–173.

[37] H.B. Bradl, Heavy Metals in the Environment: Origin, Interaction and Remediation, Elsevier, Amsterdam, 2005.

[38] V. Gupta, M. Gupta, S. Sharma, Process development for the removal of lead and chromium from aqueous solutions using red mud—An aluminium industry waste, Water Res. 35 (2001) 1125–1134.

[39] B.V. Lenntech, Lead and Water, Water Treatment Solutions, 2011. Available from: <http://www.lenntech.com/periodic/water/lead/lead-and-water.htm>.

[40] EPA, CERCLA/Superfund Orientation Manual, Document No. EPA/542/R-92/005, 1992.

[41] M. Owlad, M.K. Aroua, W.A. Wan Daud, S. Baroutian, Removal of hexavalent chromium-contaminated water and wastewater: A review, Water Air Soil Pollut. 200(1) (2009) 59–77.

[42] J. Kotaś, Z. Stasicka, Chromium occurrence in the environment and methods of its speciation, Environ. Pollut. 107(3) (2000) 263–283.

[43] Agency for Toxic Substances and Disease Registry, Editor Toxicological Profile for Chromium, Agency for Toxic Substances and Disease Registry, 1994.

[44] E.T. Snow, Effects of chromium on DNA replication in vitro, Environ. Health Perspect. 102 (1994) 41–44.

[45] A. Zhitkovich, V. Voitkun, M. Costa, Formation of the amino acid-DNA complexes by hexavalent and trivalent chromium *in vitro*: Importance of trivalent chromium and the phosphate group, Biochemistry 35(22) (1996) 7275–7282.

[46] A. Plaper, Š. Jenko-Brinovec, A. Premzl, J. Kos, P. Raspor, Genotoxicity of trivalent chromium in bacterial cells, Chem. Res. Toxicol. 15 (2002) 943–949.

[47] M.A. Barakat, New trends in removing heavy metals from industrial wastewater, Arab. J. Chem. 4 (2011) 361–377.

[48] S. Nasreen, U. Rafique, S. Ehrman, M.A. Ashraf, Hybrid mesoporous silicates: A distinct aspect to synthesis and application for decontamination of phenols, Saudi J. Biol. Sci. (2015), doi: 10.1016/j.sjbs.2015.08.014.

[49] S.S. Kim, A. Karkamkar, T.J. Pinnavaia, M. Kruk, M. Jaroniec, Synthesis and characterization of ordered, very large pore MSU-H silicas assembled from water-soluble silicates, J. Phys. Chem. B 105 (2001) 7663–7670.

[50] E. Da'na, A.H. Sayari, Adsorption of heavy metals on amine-functionalized SBA-15 prepared by co-condensation: Applications to real water samples, Desalination 285 (2012) 62–67.

[51] O.A. Fadali, E.E. Ebrahiem, Y.H. Magdy, A.A.M. Daifullah, M.M. Nassar, Removal of chromium from tannery effluents by adsorption, J. Environ. Sci. Health, Part A Environ. Sci. Eng. 9 (2005) 465–472.

[52] N. Igarashi, K.A. Koyano, Y. Tanaka, S. Nakata, K. Hashimoto, T. Tatsumi, Investigation of the factors influencing the structural stability of mesoporous silica molecular sieves, Microporous Mesoporous Mater. 59(1) (2003) 43–52.

[53] K. Cassiers, T. Linssen, M. Mathieu, M. Benjelloun, K. Schrijnemakers, P. Van Der Voort, P. Cool, E.F. Vansant, A detailed study of thermal, hydrothermal, and mechanical stabilities of a wide range of surfactant assembled mesoporous silicas, Chem. Mater. 14(5) (2002) 2317–2324.

[54] C.F. Cheng, W. Zhou, D.H. Park, J. Klinowski, M. Jargreaves, L.F. Gladden, Controlling the channel

diameter of the mesoporous molecular sieve MCM-41, J. Chem. Soc., Faraday Trans. 93 (1997) 359–363.

[55] T.R. Pauly, V. Petkov, Y. Liu, S.J.L. Billinge, T.J. Pinnavaia, Role of framework sodium versus local framework structure in determining the hydrothermal stability of MCM-41 mesostructures, J. Am. Chem. Soc. 124 (2002) 97–103.

[56] M.H. Lim, A. Stein, Comparative studies of grafting and direct syntheses of inorganic−organic hybrid mesoporous materials, Chem. Mater. 11(11) (1999) 3285–3295.

[57] L. Mercier, T.J. Pinnavaia, Direct synthesis of hybrid organic-inorganic nanoporous silica by a neutral amine assembly route: Structure-function control by stoichiometric incorporation of organosiloxane molecules, Chem. Mater. 12 (2000) 188–196.

[58] R.J.P. Corriu, E. Lancelle-Beltran, A. Mehdi, C. Reyé, S. Brandès, R. Guilard, Ordered mesoporous hybrid materials containing cobalt(ii) Schiff base complex, J. Mater. Chem. 12(5) (2002) 1355–1362.

[59] V. Antochshuk, O. Olkhovyk, M. Jaroniec, I.S. Park, R. Ryoo, Benzoylthiourea-modified mesoporous silica for mercury(II) removal, Langmuir 19 (2003) 3031–3034.

[60] O. Olkhovyk, V. Antochshuk, M. Jaroniec, Benzoylthiourea-modified MCM-48 mesoporous silica for mercury(II) adsorption from aqueous solutions, Colloids Surf. A 236 (2004) 69–72.

[61] J. Li, L. Wang, T. Qi, Y. Zhou, C. Liu, J. Chu, Y. Zhang, Different N-containing functional groups modified mesoporous adsorbents for Cr(VI) sequestration: Synthesis, characterization and comparison, Microporous Mesoporous Mater. 110 (2008) 442–450.

[62] R. Cao, E. Bråkenhielm, R. Pawliuk, D. Wariaro, M.J. Post, E. Wahlberg, P. Leboulch, Y. Cao, Angiogenic synergism, vascular stability and improvement of hind-limb ischemia by a combination of PDGF-BB and FGF-2, Nat. Med. 9(5) (2003) 604–613.

[63] T.E. Bitterwolf, Photolysis of $[(\eta^5\text{-}C_5H_5)M(Co)_2No]^+$, where M = Mn and Re, in inert ionic matrices: Evidence for nitrosyl linkage isomerism, J. Photochem. Photobiol. A: Chem. 163(1–2) (2004) 209–213.

[64] H.G. Ilkay, Isotherms and thermodynamics for the sorption of heavy metal ions onto functionalized sporopollenin, J. Hazard. Mater. 186(1) (2011) 416–422.

[65] M. Uysal, I. Ar, Removal of Cr(VI) from industrial wastewaters by adsorption. Part I: Determination of optimum conditions, J. Hazard. Mater. 149 (2007) 482–491.

[66] A. Fazal, U. Rafique, Severance of lead by acetylated and esterified spent *Camellia sinensis* powder, Am. J. Environ. Eng. 3(6) (2013) 288–296.