

Sorption of arsenic onto Vindhyan shales: Role of pyrite and organic carbon

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Batch isotherms for arsenic sorption on Vindhyan shales were compared with arsenic sorption on black cotton soil. High sorption was observed on pyrite-rich shales and the Freundlich capacity constant K_F yielded a good correlation with sediment pyrite content. Shales with high organic carbon sorbed more arsenic; however, the organic carbon-rich soil demonstrated significantly lower sorption. This difference may be due to the condensed nature of organic carbon in shale, which may have facilitated formation of organo-arsenic complexes. The pyrite content was also strongly correlated with the organic carbon content, possibly due to microbial synthesis during shale diagenesis.

ARSENIC poisoning is a serious health concern worldwide. Arsenic concentration above permissible limits is reported from many countries. Groundwater arsenic poisoning in the Bengal basin is one of the world's largest environmental calamities^{1,2} and millions of people are in a state of high risk. Although inorganic arsenic occurs in -3, 0, +3 and +5 oxidation states in aquatic systems, the +3 form is more mobile and toxic compared to the other forms³. Sorption processes largely control the migration and fate of arsenic in natural systems. Natural sediments are heterogeneous and the overall sorption is the net result of the distinctly different sorption behaviour on each constituent phase. Many geological materials have been studied for their arsenic sorption potential. Among the various sorbents, red mud^{4,5}, zeolites⁶, feldspar minerals⁷ and iron oxide and hydroxide⁸⁻¹⁰ minerals have been extensively evaluated for their arsenic sorption potential. The sorbent characteristics of pure and individual iron oxyhydroxide minerals, such as hematite, goethite and limonite on arsenic sorption have been reported by various researchers^{8,11}. The influence of sulphate, silicate and phosphate on arsenic uptake has also been studied¹².

Many researchers have focused on the sorption characteristics of pure mineral phases, but the sorption behaviour of complex aquifer materials which constitute a number of different phases, including iron oxyhydroxides, clays and different alumino silicates has hardly been reported. In a recent study of arsenite and arsenate¹³ sorption on aquifer sediments consisting of quartz, feldspar, clays and iron oxides in different proportions, it was reported that the iron oxyhy-

droxides are primarily responsible for sorption. Natural sorbents comprise of many other components besides the iron oxide phases. The effect of other constituents and factors such as organic matter content, pyrite content and surface charge distribution on natural sediments has not been reported. Also, negligible attention has been focused on shale, although it constitutes about 70% of the earth's crust. The present work focuses on the characterization of seven shale samples from the Vindhyan basin along with a sample of black cotton soil (BCS), predominant in Mumbai, and understanding their compositional dissimilarities as well as physical and chemical properties that are likely to influence arsenic sorption. The effect of various constituents on equilibrium sorption capacity is examined.

Materials and methods

Seven shale samples from the Proterozoic Vindhyan basin, Son valley, central India and a Quaternary BCS from Mumbai were characterized for their compositional variation. Descriptions for the shale samples are summarized in Table 1 on the basis of studies by Bose *et al.*¹⁴. Major element analysis was performed by conventional methods, according to Shapiro and Brannock¹⁵. Total organic carbon (TOC) was measured by a FASH EA 1112 model CHN-analyser after removal of inorganic carbon by 1:1 HNO₃ with continuous N₂ gas purging. The pyrite percentage was determined by barium sulphate precipitation method¹⁶. Sodium acetate¹⁷ and potentiometric titration method¹⁸ was followed for cation exchange capacity (CEC) and zero point charge determination, respectively.

Equilibrium studies were carried out in batch reactors at room temperature at constant ionic strength (0.01 M), pH (5.0) and sediment load (10 g/l). The pH and ionic strength were maintained constant using acetate buffer and 0.01 M NaNO₃, respectively. Arsenous oxide (As₂O₃, 99.5%) was used for the equilibrium studies. Airtight polypropylene batch reactors were prepared with different initial arsenic concentrations (C_0). The reactors were tumbled end over end at room temperature for the predetermined equilibration time. The solutions were filtered by a Whatman filter paper (No. 42), the pH was checked and the filtrate was stored at 4°C. The final aqueous phase concentration (C_e) of arsenic was determined by silver diethyldithiocarbamate method¹⁹ for various initial arsenic concentrations (C_0).

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Table 1. Specific details on shale sorbents

Group	Formation	Member	Details of samples	Sample name/ abbreviation used		
Upper Vindhyan	Bhander	Upper Bhander Sandstone	Greenish shale alternating with sandstone	Sirbu shale, SS		
		Sirbu Shale				
		Lower Bhander Sandstone				
	Rewa	Bhander Limestone	Reddish shale alternating with sandstone	Ganurgarh shale, GS		
		Ganurgarh Shale				
		Rewa Sandstone				
Kaimur	Rewa Shale	Black shale alternating with sandstone	Bijaigarh shale, BS			
	Upper Kaimur Sandstone					
	Bijaigarh Shale					
Lower Vindhyan	Rohtas	Lower Kaimur Sandstone	Black calcareous shale alternating with thin limestone beds	Rampur shale, RS		
		Rohtas Limestone				
	Kheinjua	Rampur Shale			Olive green colour shale alternating with sandstone	Olive shale, OS
		Chorhat Sandstone				
	Porcellanic	Koldaha Shale			Greenish light colour shales occurring within tuffaceous beds	Porcellanic shale, PS
		Kajrahat Limestone				
	Kajrahat	Arangi Shale			Black shales alternating with dolomites	Kajrahat shale, KS
		Deoland				

Results and discussion

Characteristics of geosorbents

Shales are siliciclastic sediments with major proportions of silica and alumina. Among the seven shales and one soil sample examined, Porcellanic shales have the highest silica content, whereas the soil has the least silica content. All the shale samples are richer in potassium oxide compared to sodium oxide, while the reverse is true for the soil. Paikaray *et al.*²⁰ have reported the detailed geochemical characteristics of the sorbents. Rampur and Kajrahat shales are significantly calcareous in nature and contain high amounts of Ca and Mg carbonates. The Rampur shale is more calcareous than the Kajrahat shale. The soil is richer in iron compared to the shales. Iron oxide content in the various shale samples varies over the range 0.7 to 3.6%.

Bijaigarh, Kajrahat and Rampur shales are pyritiferous and richer in organic carbon content compared to the other shale samples and the soil (Table 2). Pyrite crystals were reported in scanning electron microscope (SEM) images of Bijaigarh shale²¹ and were subsequently also observed in Rampur and Kajrahat shales. Pyrite enrichment possibly took place during the latter stages of diagenesis due to microbial synthesis^{22,23}. The Quaternary soil does not contain much pyrite, although it has a high organic carbon content. All the sediments show an alkaline nature, except the Bijaigarh shale (BS). The sediments are neutral or have a low density of negative surface charge in their natural state, since the pH values are close to or slightly greater than the pH_{PZC} . However, in BS the pH_{PZC} slightly exceeds the pH value. Olive shale has the highest cation exchange capacity (33.0 meq/100 g) compared to the other sorbents. The CEC value of BS is the least (17 meq/100 g).

Isotherm studies

All the eight sorbents were evaluated for their arsenic(III) sorption characteristics. Aqueous phase arsenic concentration in the batch reactors stabilized within the equilibration time of 48 h (C_e , meq/l). Over the equilibration time the pH values were relatively constant at 5 ± 0.1 . The arsenic loading on the sorbents (q_e , meq/g) was determined by mass balance. The sorption isotherm data (q_e vs C_e) were fitted to the Langmuir and Freundlich isotherm models using the statistical package SYSTAT (Systat software Asia Pacific Ltd, Bangalore, India). Nonlinear regression was performed using the Quasi Newton method. Langmuir model (eq. (1)) assumes a monolayer surface coverage, where, Q_a^0 is the sorption capacity and b is the sorption energy. Freundlich model (eq. (2)) is an empirical model allowing for multilayer adsorption, where K_F denotes sorption capacity and n the adsorption energetics.

$$q_e = \frac{Q_a^0 b C_e}{1 + b C_e}, \quad (1)$$

$$q_e = K_F C_e^n. \quad (2)$$

The experimental datapoints could be fitted by both the models as demonstrated in Figure 1a and b. However, the 95% confidence intervals (Table 3) for the Langmuir model parameters are wider compared to those for the Freundlich model parameters. The Langmuir model fits are therefore of poorer quality. The Freundlich model has been used extensively for representing sorption on heterogeneous surfaces, with variable energy sorption sites. Geosorbents are heterogeneous in nature and have numerous

Table 2. Geochemical composition of sorbents

Sorbent	Fe ₂ O ₃ (%)	FeS ₂ (%)	CEC (meq/100 g)	pH _{PZC}	TOC (%)	pH
SS	2.41	0.02	20.36	6.9	0.06	7.7
GS	3.62	0.04	20.89	6.3	0.07	8.8
BS	1.83	0.62	16.99	4.0	1.93	3.9
RS	1.32	0.46	24.43	9.2	0.65	9.4
PS	2.19	0.03	29.91	6.8	0.10	8.2
OS	1.95	0.03	33.19	6.5	0.08	7.5
KS	0.68	0.48	21.68	9.0	0.99	9.2
BCS	7.63	0.03	26.11	7.8	1.36	8.6

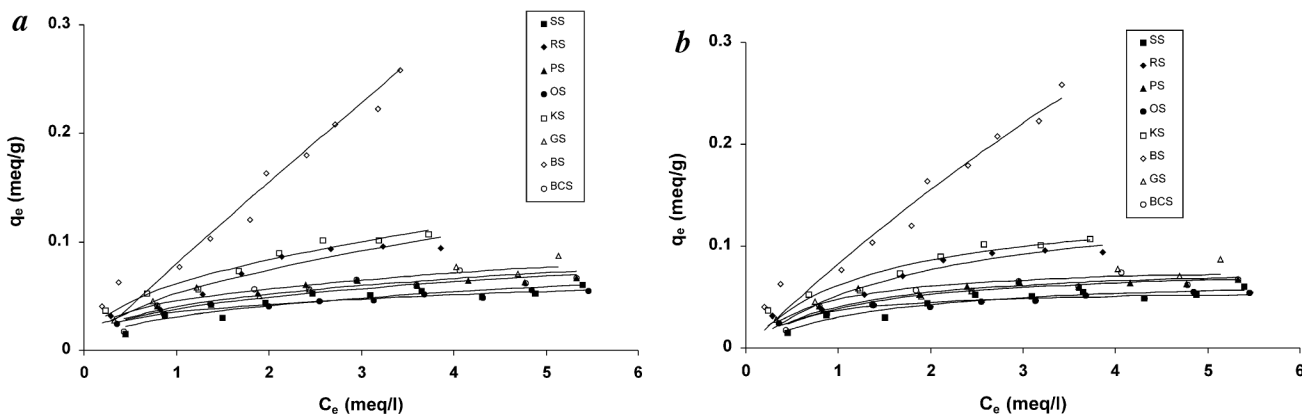


Figure 1. Freundlich (a) and Langmuir (b) model fits to data.

Table 3. Equilibrium parameters for arsenic sorption

Sorbents	Langmuir parameters				Freundlich parameters			
	Q_a^0 ($\frac{\text{meq}}{\text{g}}$)		b ($\frac{L}{\text{meq}}$)		K_F ($\frac{\text{meq}}{\text{g}}$) ($\frac{L}{\text{meq}}$) ⁿ		n	
	Mean	95% CI	Mean	95% CI	Mean	95% CI	Mean	95% CI
SS	0.071	0.056–0.087	0.743	0.243–1.242	0.031	0.024–0.037	0.397	0.232–0.561
GS	0.083	0.065–0.101	1.343	0.154–2.532	0.045	0.037–0.053	0.329	0.190–0.468
BS	1.349	–2.112–4.811	0.065	–0.131–0.261	0.091	0.068–0.114	0.797	0.541–1.054
RS	0.152	0.090–0.213	0.509	0.061–0.958	0.052	0.042–0.062	0.514	0.325–0.703
OS	0.058	0.052–0.063	1.671	0.945–2.396	0.035	0.032–0.037	0.271	0.213–0.329
PS	0.081	0.068–0.095	0.916	0.403–1.429	0.038	0.031–0.046	0.364	0.205–0.522
KS	0.144	0.095–0.192	0.748	0.099–1.397	0.061	0.053–0.068	0.451	0.326–0.575
BCS	0.083	0.068–0.098	0.944	0.359–1.530	0.040	0.032–0.048	0.359	0.197–0.521

constituent phases. Each constituent phase may potentially take part in the sorption interactions, giving rise to heterogeneous surface behaviour.

Influence of sorbent geochemistry on total sorption

The geosorbents show variable sorption affinities for As(III) as depicted by the model parameters listed in Table 3. Due to the wide confidence interval of Langmuir model parameters, the Freundlich model parameters are compared across all the sorbents. The Freundlich constant, K_F , represents the sorption capacity and a higher K_F suggests greater sorp-

tion. Among the seven shale samples, BS shows the highest sorption capacity and SS the least. The soil exhibits very low sorption capacity for arsenic.

Among the various constituents, iron oxyhydroxides are reported as efficient arsenic adsorbents since they form inner sphere complexes with arsenic. However, contrary to expectation, the sorption capacity does not correlate with the Fe₂O₃ content of the sorbents as depicted by the random scatter of datapoints in Figure 2a. The soil with the highest Fe₂O₃ content does not show high sorption capacity. Instead, BS having much lower Fe₂O₃ content shows the highest sorption capacity. A detailed mineralogical

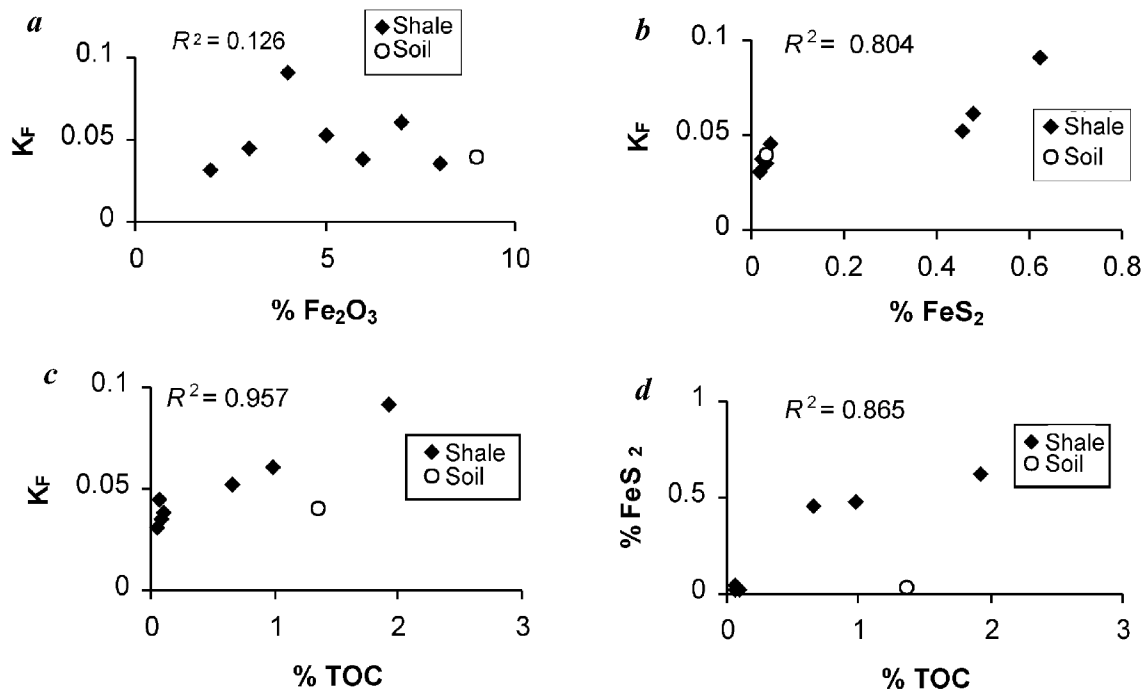


Figure 2. Correlations for sorption capacity parameter, K_F with iron oxide (a), Pyrite (b), Total carbon content (TOC) (c) and for pyrite with TOC (d).

Table 4. Mineralogical composition identified by XRD

SS	Quartz, illite, halloysite, muscovite, calcite
GS	Quartz, albite, anorthite, muscovite, montmorillonite, hematite, phlogopite, calcite, illite, zeolite, apatite
BS	Quartz, muscovite, illite, montmorillonite, pyrite, calcite
RS	Quartz, orthoclase, muscovite, illite, montmorillonite, biotite, phlogopite, calcite, dolomite, halloysite
PS	Quartz, orthoclase, muscovite, illite, calcite, halloysite
OS	Quartz, muscovite, illite, halloysite, montmorillonite
KS	Quartz, muscovite, montmorillonite, illite, calcite, halloysite, dolomite
BCS	Quartz, albite, illite, vermiculite, montmorillonite, calcite, biotite

identification based on X-ray diffraction (XRD) analysis indicated the absence of any iron oxides/hydroxides in these sorbents, except for the Ganurgarh shale (GS; Table 4). The XRD spectra for GS depicted a hematite peak of low relative intensity (3.0%). The presence of Fe^{3+} oxides is also evident from the red colour of this rock. Oxidation of the ferrous ions (Fe^{2+}) to ferric form (Fe^{3+}) may have taken place in the depositional environment²⁴. The Fe_2O_3 on the other samples may have resulted from Fe-bearing clay, micas and other trace minerals and/or dissolved iron in the sediments. Thus, although it is believed that hematite may have caused some arsenite sorption on GS, arsenite sorption on the other shales is not due to iron oxide minerals. The BS, RS and KS yielded significantly higher sorption capacities compared to GS, although they did not contain hematite or any other iron oxyhydroxide minerals. Thus, the influence of some other constituent dominates the sorption phenomenon in these sorbents.

The arsenic sorption capacity does not demonstrate any correlation with the CEC and pH_{PZC} for the sorbents stud-

ied. The system pH of 5.0 is lower than the pH_{PZC} of the shales other than BS, such that a net positive charge possibly existed on the surfaces. BS possibly had a net negative surface charge. At the system pH of 5.0, As(III) is present as H_3AsO_3 , a neutral species²⁵. The sorption of this neutral species is likely to be unaffected by the net surface charge on these sorbents.

Pyrite (FeS_2) constitutes a minor fraction of the total composition, however, the pyrite content when compared with the sorption capacity yields a significant correlation with a high R^2 value as depicted in Figure 2b. The pyrite fraction is found to have a dominant impact on overall sorption. BS, with the highest FeS_2 content, demonstrates the highest sorption capacity. GS, in spite of its low pyrite content, yields a relatively higher sorption capacity possibly due to the presence of hematite. Arsenic is associated with sulphides as realgar (AsS), and orpiment (As_2S_3) and with iron sulphides as arsenopyrite ($FeAsS$). Pyrites in sediments may interact with dissolved arsenic forming surface complexes of arsenopyrites through slow surface complexa-

tion reactions²⁶. Precipitation of FeAsS has also been reported by Bostic and Fendorf²⁷ on troilite (FeS) and pyrite (FeS₂) surfaces.

A good correlation between sorption capacity parameter, K_F , and sediment organic carbon content (TOC) is also observed, particularly for the shales (Figure 2c). This correlation coefficient is even higher than that for pyrites. Although the soil has high TOC, it demonstrates significantly lower sorption capacity. It appears that the organic matter in the soil is not involved in sorbent–sorbate interaction processes for arsenic sorption. The nature of organic matter in the soil is significantly different from that of the shale samples belonging to a ~1.6 Ga-old sedimentary basin. The soil belongs to a comparatively recent age (<1.0 Ma). Influence of organic matter on heavy metal sorption is widely reported^{28,29} based on sorption equilibrium studies; however, its role on arsenic sorption has not been demonstrated earlier, although recent studies suggest the tendency for arsenic to associate with organic matter. Baruah *et al.*³⁰ reported the association of arsenic species with aquifer carbonaceous materials in four Northeastern states of India. High arsenic concentrations were measured in sediments richer in organic carbon, and arsenic was found both in association with the aromatic as well as the hydrogenetic fraction of organic matter, in the form of organo-arsenic complexes. It is reported that the complexation of arsenic with natural organic matter in the aqueous phase enhances its mobility and the degree of complexation varies widely with the nature and origin of organic matter³¹. Detailed investigation on the presence of different functional groups of carbonaceous matter and the type of organic matter may enhance the understanding of arsenic speciation onto the organic carbon fraction of these geosorbents. Our observation suggests that condensed organic matter in sediments can cause significant arsenic uptake, whereas the amorphous organic matter incorporated in recent soils does not have much impact on arsenic sorption.

Although a good correlation exists between sorption capacity and TOC, it may be noted that the TOC is strongly correlated with the pyrite content, particularly for the pyrite-rich shales (Figure 2d). This can be attributed to microbial synthesis of pyrites during diagenesis^{20,21}. Thus, a clear cause–effect relationship for sorption cannot be established based on this study. It is possible that both pyrites and organic carbon individually contributed to sorption by formation of surface precipitates of arsenopyrites and organo-arsenic complexes, respectively. Else, it is also possible that only pyrites controlled the overall sorptive interactions, and the organic carbon content demonstrated a correlation with the sorption capacity parameter simply due to its correlation with pyrites and vice versa.

Summary

Cation exchange capacity, major oxides, point of zero charge and sediment pH did not have much influence on total sorp-

tion. TOC and pyrite content dominated the arsenic sorption phenomenon, although they represent minor components with respect to the whole rock geochemistry. The pyrites may be forming arsenopyrite-type surface precipitates on interaction with aqueous phase arsenic, thus favouring arsenic sorption. The condensed and hard organic matter in shale is found to demonstrate a significantly higher correlation with their respective sorption capacities, possibly by forming organo-arsenic complexes. The presence of pyrites and organic matter in aquifers may significantly affect the mobility of arsenic species.

- Mandal, B. K. *et al.*, Arsenic in groundwater in seven districts of West Bengal, India – The biggest arsenic calamity in the world. *Curr. Sci.*, 1996, **70**, 976–986.
- Saha, K. C., Review of arsenicosis in West Bengal, India – A clinical perspective. *Crit. Rev. Environ. Sci. Technol.*, 2003, **30**, 127–163.
- B'Hymer, C. and Caruso, J. A., Arsenic and its speciation analysis using high-performance liquid chromatography and inductively coupled plasma mass spectrometry. *J. Chromatogr. A*, 2004, **1045**, 1–13.
- Altundođan, H. S., Altundođan, S., Tmen, F. and Bildik, M., Arsenic removal from aqueous solutions by adsorption on red mud. *Waste Manage.*, 2000, **20**, 761–767.
- Altundođan, H. S., Altundođan, S., Tmen, F. and Bildik, M., Arsenic adsorption from aqueous solution by activated red mud. *Waste Manage.*, 2002, **22**, 357–363.
- Elizalde-Gonzalez, M. P., Mattusch, J., Einicke, W. D. and Wennrich, R., Sorption on natural solids for arsenic removal. *Chem. Eng. J.*, 2001, **81**, 187–195.
- Prasad, G., Removal of As(V) from aqueous systems by adsorption onto some geological materials. In *Arsenic in the Environment* (ed. Nriagu, J. O.), John Wiley, 1994, pp. 133–154.
- Bowell, R. J., Sorption of arsenic by iron oxides and oxyhydroxides in soils. *Appl. Geochem.*, 1994, **9**, 279–286.
- Raven, K. P., Jain, A. and Loeppert, R. H., Arsenite and arsenate adsorption on ferrihydrite: Kinetics, equilibrium and adsorption envelopes. *Environ. Sci. Technol.*, 1998, **32**, 344–349.
- Richmond, W. R., Loan, M., Morton, J. and Parkinson, G. M., Arsenic removal from aqueous solution via ferrihydrite crystallization control. *Environ. Sci. Technol.*, 2004, **38**, 2368–2372.
- Zhang, W., Singh, P., Paling, E. and Delides, S., Arsenic removal from contaminated water by natural iron ores. *Miner. Eng.*, 2004, **17**, 517–524.
- Meng, X., Bang, S. and Korfiatis, G. P., Effect of silicate, sulphate and carbonate on arsenic removal by ferric chloride. *Water Res.*, 2000, **34**, 1255–1261.
- Carrillo, A. and Drever, J. I., Adsorption of arsenic by natural aquifer material in the San Antonio–El Triunfo mining area, Baja California, Mexico. *Environ. Geol.*, 1998, **35**, 251–257.
- Bose, P. K., Sarkar, S., Chakrabarty, S. and Banerjee, S., Overview of the Meso to Neoproterozoic evolution of the Vindhyan basin, central India. *Sed. Geol.*, 2001, 395–419.
- Shapiro, L. and Brannock, W. W., Rapid analysis of silicate rocks: A contribution to geochemistry, US Dept. of Interior, Washington, 1956, pp. 19–53.
- Furman, N. H. (ed.), *Standard Methods of Chemical Analysis*, Robert E. Krieger Publishing Company, Malabar, Florida, 1962, p. 1401.
- Jackson, M. I., *Soil Chemical Analysis*, Prentice Hall, Englewood Cliffs, NJ, 1958, p. 498.
- Smith, E. J., Surface complexation modeling of metal removal by recycled iron sorbent. *J. Environ. Eng.*, 1998, 913–919.

19. Standard methods for examination of water and waste water, American Public Health Association, 1998.
20. Paikaray, S., Banerjee, S. and Mukherji, S., Adsorption behaviour of heavy metal pollutants onto shales and its correlation with shale geochemistry. *Environ. Geol.*, 2005 (available online).
21. Paikaray, S. and Banerjee, S., SEM observations of organic carbon-rich Bijaygarh shales, Vindhyan Supergroup (~1.8–0.6 Ga), central India and their implications. XXVI Annual Conference on Electron Microscopy and Allied Fields, 2003, pp. 119–120.
22. Berner, R. A., Sedimentary pyrite formation. *Am. J. Sci.*, 1970, **268**, 1–23.
23. Leventhal, J. S., Metal-rich black shales: Formation, economic geology and environmental method considerations. In *Shales and Mudstones, Vol. II* (eds Schieber, J., Zimmerle, W. and Sethi, P. S.), E. Schweizerbart'sche Verlagsbuchhandlung (Nägele U. Obermiller), Stuttgart, 1998, pp. 256–282.
24. McBride, E. F., Chemisorption of Cd²⁺ on calcite surfaces. *J. Sed. Petrol.*, 1974, **44**, 760–773.
25. Peterson, M. I. and Carpenter, R., Biogeochemical processes affecting total arsenic and arsenic species distributions in an intermittently anoxic fjord. *Mar. Chem.*, 1983, **12**, 295–321.
26. Jingtai, H. and Fyfe, W. S., Arsenic removal from water by iron-sulfide minerals. *Chin. Sci. Bull.*, 2000, **45**, 1430–1434.
27. Bostick, B. C. and Fendorf, S., Arsenite sorption on troilite (FeS) and pyrite (FeS₂). *Geochim. Cosmochim. Acta*, 2003, **67**, 909–921.
28. Lee, S., Chang, L., Yang, H., Chen, C. and Liu, M., Adsorption characteristics of lead onto soils. *J. Hazard. Mater.*, 1998, **A63**, 37–49.
29. Schmitt, D., Taylor, H. E., Alken, G. R., Roth, D. A. and Frimmel, F. H., Influence of natural organic matter on the adsorption of metal ions onto clay minerals. *Environ. Sci. Technol.*, 2002, **36**, 2932–2938.
30. Baruah, M. K., Kotoky, P., Baruah, J., Borah, G. C. and Bora, P. K., Arsenic association and distribution in carbonaceous materials in northeastern India. *Curr. Sci.*, 2003, **85**, 204–208.
31. Redman, A. D., Macalady, D. L. and Ahmann, D., Influence of natural organic matter on sorption of arsenic oxyanions onto metal oxides. GSA Annual Meeting, Boston, 2001.

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