

Selective Sorption of Chromium from Tannery Wastes by Hybrid Cation Exchange Resin

TAUQEER AHMAD^{1,2,*}, SYED MUSTAFA², ABDUL NAEEM², FAROOQ ANWAR¹, KHIZAR HUSSAIN SHAH² and TAHIR MEHMOOD¹

¹Department of Chemistry, University of Sargodha, Sargodha-40100, Pakistan

²National Centre of Excellence in Physical Chemistry, University of Peshawar, Peshawar-25120, Pakistan

*Corresponding author: E-mail: tskp72@yahoo.com

Received: 8 October 2013;

Accepted: 16 January 2014;

Published online: 5 July 2014;

AJC-15473

A hybrid cation exchanger of a strong acid exchanger Amberlite IR-120 with iron hydroxide is used for the removal of chromium(III) from the tannery wastes. The hybrid ion exchanger has been found to have higher sorption capacity for the chromium(III) ions as compared to Amberlite IR-120 and iron hydroxide which is further enhanced with the increase in temperature. Chromium speciation analyses indicate that the main chromium species being sorbed are CrSO_4^+ and Cr^{3+} , as they are the dominant species present in spent tannery bath solution. The higher sorption by the hybrid ion exchanger is due to the presence of two different types of the sites $-\text{SO}_3\text{H}$ and $-\text{OH}$, and also due to the Donnan sorption effect of the polystyrene anions. The Langmuir sorption isotherm is found applicable to the experimental data. Isothermic heats of adsorption are found to be positive and smaller than 80 kJ mol^{-1} indicating that the sorption process is endothermic and ion exchange in nature.

Keywords: Chromium(III), Sorption, Tannery wastes, Ion exchange, Hybrid cation exchanger.

INTRODUCTION

Chromium is extensively used in various industries and their effluents are the main source of aquatic and environmental pollution. In aqueous solutions chromium usually exists in the form of chromium(III) and chromium(VI). Chromium(VI) is more soluble, mobile and toxic than chromium(III). Further, chromium can be easily transformed from chromium(III) to chromium(VI) due to the presence of strong oxidizing agents like, MnO_2 or oxygen concentration greater than $10^{-6} \text{ atm}^{1,2}$. Due to the toxic effects of chromium World Health Organization (WHO) and Environmental Protection Agency (EPA) have setup a maximum level of 0.05 mg L^{-1} for Cr(VI) and 0.17 mg L^{-1} for chromium(III) in drinking water³. National environmental quality standards of Pakistan has also set the maximum level of total chromium to 1.0 mg L^{-1} in the effluents⁴.

A number of methods have been developed for the treatment of industrial effluents containing chromium like; electro dialysis, membrane process, solvent extraction, bio-separation, precipitation, sorption, ion exchange *etc.*, from which ion exchange process is preferred due to its advantages over other technologies of being rapid, low cost, highly selective and meeting the discharge specifications⁵⁻⁹.

Among the two stable chromium species, the researchers have paid a high attention towards the removal of chromium(VI) from aqueous solutions and wastewaters due to its higher

toxicity¹⁰⁻¹⁷. However, only a few investigations dealing with chromium(III) removal were found in the literature^{6,18-22}.

In recent years, metal oxides/hydroxides are used as grafting materials for the ion exchange resins. These grafted exchangers known as hybrid ion exchangers are durable, mechanically strong and possess excellent attrition resistance properties^{23,24}. A number of hybrid exchangers have been prepared and used for sorption purposes. Pan *et al.*²⁵ impregnated a polymeric cation exchanger D-001 with hydrated ferric oxide to obtain a hybrid sorbent HFO-001 which was found to be highly efficient and selective for the sorption of lead, copper and cadmium from a solution containing excess of calcium ions. Dong *et al.*²⁴ and Zhu *et al.*²⁶ had loaded MnO_2 on ion exchangers and investigated that these exchangers were effective for the removal of trace amount of lead and cadmium in the presence of alkali and alkaline earth metals. The hybrid ion exchangers containing hydrated ferric oxide nanoparticles were employed for the removal of arsenic and phosphate²⁷⁻³⁰.

In the present study, iron hydroxide and hybrid ion exchangers of Amberlite IR-120 and Amberlite IRA-400 with iron hydroxide are prepared and employed for the removal of chromium(III) ions from the spent tannery bath (STB) solution. A comparison of the results has been made to evaluate the selectivity behavior of these adsorbents for chromium(III) ions. The experimental data is explained with the Langmuir isotherm model.

EXPERIMENTAL

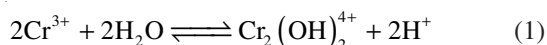
All the chemicals used were of analytical reagent grade and used without further purification. Synthetic spent tannery bath solution was prepared according to the composition given in literature^{31,32}. The solutions were prepared in deionized water (Milli-Q water purification system Millipore USA) and Pyrex glass apparatus was used throughout the study. A strong acid cation exchange resin Amberlite IR-120 and a strong base anion exchange resin Amberlite IRA-400 were used as sorbents.

The hybrid cation and anion exchangers in the form of iron hydroxide were prepared using the method reported elsewhere^{23,28-31} while, iron hydroxide was prepared in the laboratory according to the method reported by Mustafa *et al.*³³. The total iron content of the hybrid ion exchangers was measured by acid digestion in 10 % sulfuric acid and then using atomic absorption spectrophotometer (model: Perkin-Elmer A Analyst 800). The surface area of the hybrid cation exchanger was measured by using surface area and pore size analyzer Nova 1200e (Quantachrome Model No. N12-25E, USA), while the point of zero charge (pzc) of the hybrid cation exchanger was determined using the method reported by Kinniburgh *et al.*³⁴.

Ion exchange studies: Sorption of chromium(III) from spent tannery bath solution by the ion exchangers was studied as a function of temperature (293, 303, 313 and 323 K) in the concentration range of 1.923-84.615 mmol L⁻¹ through batch experiments. 30 mL of spent tannery bath solution was added into conical flasks of 50 mL containing 0.2 g of the adsorbent. The flasks were sealed and placed in a shaking water bath at desired temperature (293-323 K) at 100 rpm for 4 h. The resins were separated by filtration after 4 h and the aliquots were analyzed for chromium concentration in solution using visible spectrophotometer model: Vis-1100 and atomic absorption spectrophotometer model: Perkin-Elmer A Analyst800^{6,35}. pH of the solutions were measured with a pH-meter (BOECO BT-600, Germany) using a combination glass electrode and automatic temperature compensation (ATC) temperature probe NTC30 K.

RESULTS AND DISCUSSION

Speciation of chromium in the spent tannery bath solution: The chromium speciation (%) in the spent tannery bath solutions at 293 and 323 K using computer program visual Minteq is given in Table-1. It can be seen that at 293 K and at both the pH values 2 and 3 the major chromium species present in the spent tannery bath solution are CrSO₄⁺ and Cr³⁺. However, by increasing the temperature to 323 K the major chromium species become Cr³⁺ and at pH 3, indicating an increase in the hydrolysis reaction as



Characterization of hybrid cation exchange resins (HCIX): The BET surface areas of Amberlite IR-120 and its hybrid with Fe(OH)₃ are found to be 38.46 and 57.36 (m²/g). The PZC value of the hybrid ion exchanger can be deduced from the plot of the change in pH (ΔpH) versus initial pH (pHi) as shown in Fig. 1 and found to be 7.7. The PZC value

TABLE-1
CHROMIUM SPECIATION IN THE SYNTHETIC SPENT TANNERY BATH SOLUTION WITH VISUAL MINTEQ

Species	% Speciation			
	pH = 2		pH = 3	
	293 K	323 K	293 K	323 K
Cr ³⁺	35.907	29.781	26.686	4.155
Cr(OH) ₂ ²⁺	0.239	0.942	1.779	1.524
CrOHSO ₄ (aq)	0.088	1.278	0.877	4.704
CrSO ₄ ⁺	61.727	42.000	61.757	15.563
CrCl ²⁺	1.913	3.348	1.428	0.559
Cr ₂ (OH) ₂ SO ₄ ²⁺	–	0.272	0.125	2.202
Cr ₂ (OH) ₂ (SO ₄) ₂ (aq)	–	0.057	0.035	1.050
Cr ₂ (OH) ₄ ⁴⁺	0.125	22.11	6.897	59.882
Cr ₃ (OH) ₄ ⁵⁺	–	0.211	0.415	10.421

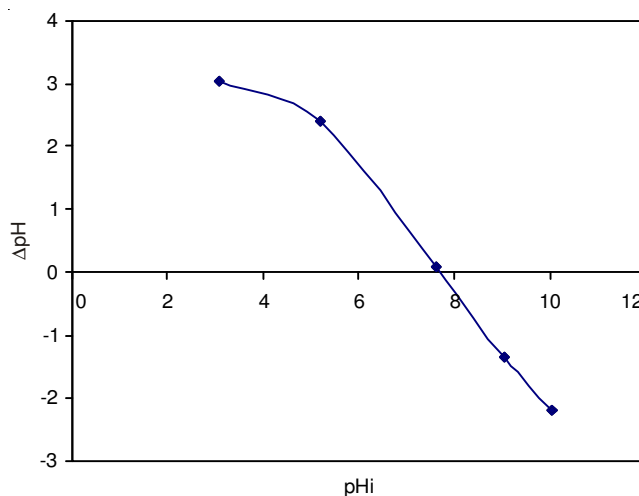


Fig. 1. Plot of ΔpH for hybrid exchangers as a function of pHi

found is very close to the values reported by Kosmulski³⁶ for iron hydroxide. The iron content in the hybrid cation exchanger is found to be 7.89 %.

Sorption studies: Sorption of Cr(III) on hybrid ion exchange resin of Amberlite IR-120 with Fe(OH)₃ is studied at 293 and 323 K and the results obtained are shown in Fig. 2. It is observed that the hybrid cation exchanger has better chromium removal capacity as compared to the virgin exchanger at both the temperatures under investigation. The higher sorption capacity of the hybrid cation exchanger is due to the presence of the two different types of groups, -SO₃H in the polystyrene matrix and -OH on the surface of the iron hydroxide. It is reported in literature that Cr³⁺ can be sorbed by the -SO₃H groups of the cation exchanger according to the reaction (2)¹⁹.



where R is the organic part of the exchanger, M is the cation while, n is the number of hydrogen ions exchanged.

From the chromium speciation given in Table-1, one would expect the sorption of being preferred overall the other chromium species as it is univalent and has the highest concentration. The involvement of the -SO₃H of the hybrid ion exchanger may also be assumed from the FTIR data given in Fig. 3. As can be seen, the precipitation of Fe(OH)₃ has no effect on the IR bands of OH vibrations at 3600-3200 cm⁻¹ and

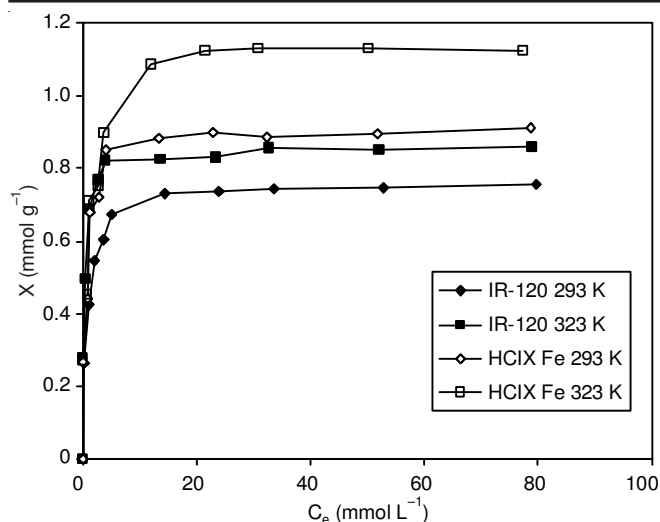


Fig. 2. Sorption isotherms for chromium(III) removal from spent tannery bath solutions by different exchangers at 293 and 323 K

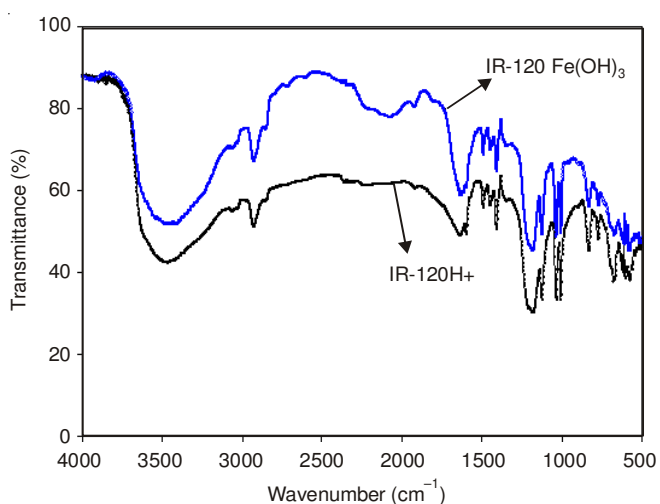
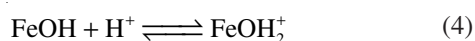


Fig. 3. FTIR spectra of Amberlite IR-120 H⁺ and its hybrid with Fe(OH)₃

the sulfonate band at 1220-1130 cm⁻¹. The sulfonate bands have almost the same intensity in both the forms of ion exchanger, showing that the -SO₃H groups of the exchanger are not blocked by the precipitation of the iron hydroxide in the matrix of the parent resin. Similar IR bands for Amberlite IR-120 resin were reported by Jha *et al.*³⁷

As far as iron hydroxide is concerned, many researchers had reported that the iron hydroxide in aqueous solutions developed surface -OH groups, which are then responsible for the uptake of metal cations according to reaction (3)³⁸⁻⁴⁰. Further as the pH values of the spent tannery bath solutions are below the pzc of the hybrid ion exchanger *i.e.*,^{7,7}, the protonation reaction (4) may also be assumed to take place in addition to the chromium sorption by the iron hydroxide.



To determine the contribution of the iron hydroxide, Cr(III) sorption experiments were also performed at 293 and 323 K. It can be noted that the sorption capacity of the iron hydroxide increases with the increase in temperature. It can

also be seen from Fig. 2 that iron hydroxide has low sorption capacity as compared to the organic ion exchanger Amberlite IR-120. If it is assumed that the sorption by the hybrid cation exchanger is additive in nature, then the increase in the sorption of Cr(III) by it would be too small, as firstly the amount of the iron hydroxide present in the exchanger is only 7.89 % and secondly as is revealed by the IR spectra (Fig. 3), the precipitation of iron hydroxide has almost no effect on the -SO₃H groups of the exchanger. Thus, the increased sorption of Cr(III) by hybrid cation exchanger can only be the result of the well known Donnan sorption effect. This effect enhances the sorption of the counter ions Cr(III) in the present case while excluding the co-ions from the hybrid cation exchanger. The role of this effect is also supported by the data obtained for the Cr(III) sorption on hybrid anion exchanger, when the iron hydroxide is precipitated in the anion exchange resin Amberlite IRA-400, replacing the non diffusible polystyrene anion (R⁻) into the corresponding cation (R⁺). The hybrid anion exchanger is found to have very low sorption capacity for Cr(III) ions *i.e.*, 0.0073 mmol g⁻¹ at 293 K, which as expected is even smaller than the iron hydroxide. This low sorption value is again due to the Donnan exclusion effect *i.e.*, the exchanger in the present case would exclude the cations in comparison to anions from the solid phase of the exchanger. Similar enhanced sorption by the hybrid ion exchangers due to the Donnan sorption effect had also been reported elsewhere^{25,27,28,41}.

The pH changes accompanying the chromium sorption reactions by the hybrid cation exchanger are given in Table-2. The corresponding PZC value being 7.7 indicates that at 293 K the chromium sorption reaction (3) predominates the surface protonation reaction (4), while the converse is true when temperature is increased to 323 K. This assumption can also be drawn from the fact that the equilibrium pH values at 293 K are lower than 323 K at low Cr(III) concentrations. Further at higher concentrations of chromium and at both the temperatures the changes in pH are negligibly small showing that the increased amount of hydrogen ions released by the exchanger as a result of chromium sorption according to reaction (3) are consumed by the surface protonation reactions of the oxides/hydroxides according to reaction (4). It is generally known that the iron hydroxide has high affinity for the protons at low pH values⁴²⁻⁴⁵.

TABLE-2
EQUILIBRIUM pH VALUES FOR THE SORPTION OF CHROMIUM(III) FROM STB SOLUTION BY HCIXS

C _o (mmol L ⁻¹)	pH _i	pH _e			
		Amberlite IR-120		HCIX Fe(OH) ₃	
		293 K	323 K	293 K	323 K
1.923	3.656	1.999	2.792	5.126	6.057
3.846	3.419	1.999	1.974	4.597	4.751
5.769	3.322	1.974	1.939	4.173	4.588
7.692	3.164	1.952	1.939	3.782	4.397
9.615	3.131	1.952	1.940	3.681	3.994
19.231	3.103	1.951	1.980	3.288	3.789
28.846	3.092	1.979	2.021	3.107	2.989
38.462	3.071	2.007	2.039	3.050	2.914
57.692	3.063	2.154	2.179	3.003	2.900
84.615	3.000	2.213	2.263	2.973	2.893

Langmuir isotherm is frequently used to describe the equilibrium ion exchange relationship between the solid and liquid phases. In the present situation, it relates the chromium uptake per unit weight of adsorbent X , to the equilibrium adsorbate concentration in the solution C_e . The linear form of Langmuir isotherm is described as

$$\frac{C_e}{X} = \frac{1}{K_b X_m} + \frac{C_e}{X_m} \quad (4)$$

where X_m is the maximum sorption capacity and K_b is the binding constant related to free energy of the exchange reaction. The sorption model is found applicable to the experimental data for Cr(III) sorption by iron hydroxide, Amberlite IR-120 and the hybrid cation exchanger with $R^2 > 0.99$. The corresponding Langmuir parameters are given in Table-3. It is observed that the X_m values are found to increase with the increase in temperature. In accordance with the data in the isotherms, the X_m values for hybrid cation exchanger are higher than the iron hydroxide and the cation exchanger Amberlite IR-120. The X_m values found here for hybrid cation exchanger are higher than the X_m values reported in literature for Cr(III) ions as can be seen from the data given in Table-4^{38,46-48}.

Temperature (K)	IR-120 H ⁺		Fe(OH) ₃		HCIX Fe(OH) ₃	
	X _m	K _b	X _m	K _b	X _m	K _b
293	0.758	1.481	0.113	3.582	0.914	1.691
323	0.858	3.108	0.257	1.302	1.143	1.340

X_m (mmol g⁻¹), K_b (L mmol⁻¹)

Sorbents	X _m (mmol g ⁻¹)				Ref.
	293 K	303 K	313 K	323 K	
Wine processing sludge	0.201	0.259	0.296	0.315	38
Composite alginate-goethite beads	0.398	0.463	0.487		46
Activated carbon, ATFAC	0.211	0.235	0.310		47
Activated carbon fabric cloth	0.693	0.761	0.775		
Activated carbon	1.09	1.08	0.511	0.836	48
Norit carbon (oxidized)	0.492	1.010	1.019	0.883	

The results in Table-4 indicate that the K_b values which are a measure of the energy of sorption are found to be higher for iron hydroxide as compared to the hybrid and sulfonic acid exchanger Amberlite IR-120, as the replacement of H⁺ by the chromium cations requires a greater amount of energy in iron hydroxide than in the sulfonic acid exchanger. Further, they are found to decrease with the increase of temperature for iron hydroxide and increase slightly for Amberlite IR-120. The decrease in the K_b values in iron hydroxide loaded exchanger, similar to iron hydroxide points towards the greater role of the Donnan sorption by iron hydroxide, played in the overall take up the chromium ions by the hybrid cation

exchanger, as suggested earlier. Similar decrease in the K_b values with temperature was found for trivalent chromium removal from tannery effluents on activated carbon by Mohan *et al.*⁴⁷.

Isosteric heat of sorption: The isosteric heat of sorption for chromium(III) sorption by iron hydroxide, Amberlite IR-120 and hybrid cation exchanger can be calculated using Clausius-Clapeyron equation (6)

$$\Delta H_r = 2.303R \left(\frac{T_1 T_2}{T_1 - T_2} \right) \log \left(\frac{C_2}{C_1} \right)_\theta \quad (6)$$

where ΔH_r is the isosteric heat of adsorption in kJ mol⁻¹, R is the gas constant and C_1 and C_2 are the equilibrium concentrations of the chromium ions at the temperatures T_1 and T_2 at constant amount of adsorption, respectively. The values of ΔH_r are plotted against the extent of adsorption in Fig. 4. As can be seen, the values are positive and below 80 kJ mol⁻¹ which indicate that the process is endothermic in nature and controlled by ion exchange mechanism⁴⁹⁻⁵⁰.

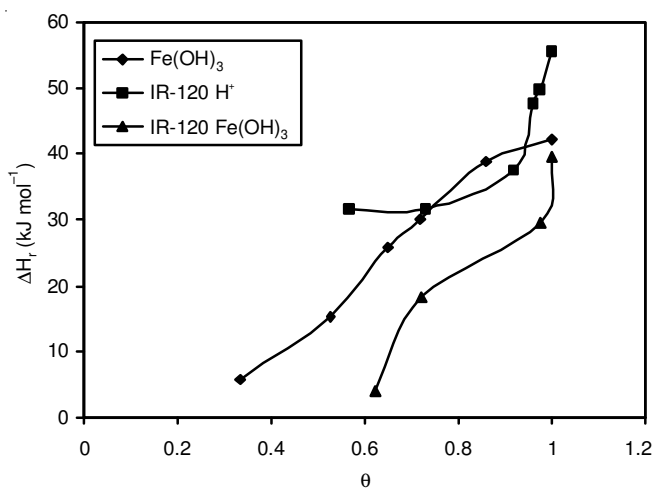


Fig. 4. Plot of θ vs. ΔH_r for different adsorbents

Further, the low values of ΔH_r in case of iron hydroxide and hybrid cation exchanger and their increase with the extent of adsorption show the proton competition for the surface -OH groups according to reaction (4). According to Machesky and Anderson⁵¹ the proton sorption reaction is exothermic in nature and the heat evolved is 38.9 kJ mol⁻¹. The increase in chromium(III) sorption would reduce the proton sorption by the iron hydroxide, resulting in an increase in the isosteric heat of the sorption. The isosteric heat data also reveal that the ion exchange sites in Amberlite IR-120 more or less homogeneous in nature. The sudden jump in the ΔH_r at higher θ values points towards the steric hindrance for the incoming chromium ions both in case of the cation exchanger Amberlite IR-120 and its hybrid. This hindrance is less pronounced in case of the hybrid cation exchanger as a result of the Donnan sorption effect.

Conclusion

The aim of the present investigation is to find the sorption behaviour of iron hydroxide, Amberlite IR-120 and hybrid cation exchanger of Amberlite IR-120 with iron hydroxide for the removal of chromium(III) from tannery wastes. The

results show that the hybrid cation exchanger has higher sorption capacity than iron hydroxide and Amberlite IR-120. From the Langmuir constants it is concluded that the hybrid cation exchanger is more selective for the removal of chromium(III) from spent tannery bath solution. The increased sorption by the hybrid cation exchanger is due to the Donnan sorption effect. Langmuir equation is found applicable to the sorption data for all the sorbents under investigation. From the isosteric heat of sorption, it is concluded that the sorption process is endothermic and controlled by the ion exchange mechanism. The low value of the isosteric heat of sorption of the cation exchanger reveal the competitive nature of the chromium (III) sorption in case of iron hydroxide and hybrid cation exchanger.

ACKNOWLEDGEMENTS

The authors greatly acknowledged National Centre of Excellence in Physical Chemistry, University of Peshawar, Pakistan and the Department of Chemistry, University of Sargodha, Pakistan for providing facilities to accomplish this research work.

REFERENCES

- I. Tadesse, S.A. Isoaho, F.B. Green and J.A. Puhakka, *Bioresour. Technol.*, **97**, 529 (2006).
- A.D. Apte, S. Verma, V. Tare and P. Bose, *J. Hazard. Mater.*, **121**, 215 (2005).
- I. Narin, A. Kars and M. Soylak, *J. Hazard. Mater.*, **150**, 453 (2008).
- The Gazette of Pakistan, in S.R.O. (2000), vol. (1), pp. 549.
- S. Rengaraj, K.-H. Yeon and S.-H. Moon, *J. Hazard. Mater.*, **87**, 273 (2001).
- S. Mustafa, K.H. Shah, A. Naeem, M. Waseem and M. Tahir, *J. Hazard. Mater.*, **160**, 1 (2008).
- V. Sarin, T.S. Singh and K.K. Pant, *Bioresour. Technol.*, **97**, 1986 (2006).
- S. Kocaoba and G. Akcin, *Talanta*, **57**, 23 (2002).
- J.A.S. Tenorio and D.C.R. Espinosa, *Waste Manage.*, **21**, 637 (2001).
- S. Mustafa, H. Bashir, N. Rehana and A. Naeem, *React. Funct. Polym.*, **34**, 135 (1997).
- B. Galán, D. Castañeda and I. Ortiz, *Water Res.*, **39**, 4317 (2005).
- F. Gode and E. Pehlivan, *J. Hazard. Mater.*, **119**, 175 (2005).
- A.A. Atia, *J. Hazard. Mater.*, **137**, 1049 (2006).
- T. Shi, Z. Wang, Y. Liu, S. Jia and D. Changming, *J. Hazard. Mater.*, **161**, 900 (2009).
- E. Pehlivan and S. Cetin, *J. Hazard. Mater.*, **163**, 448 (2009).
- E. Korngold, N. Belayev and L. Aronov, *Sep. Purif. Technol.*, **33**, 179 (2003).
- S.H. Lin and C.D. Kiang, *Chem. Eng. J.*, **92**, 193 (2003).
- F. Gode and E. Pehlivan, *J. Hazard. Mater.*, **100**, 231 (2003).
- S.-Y. Kang, J.-U. Lee, S.-H. Moon and K.-W. Kim, *Chemosphere*, **56**, 141 (2004).
- S. Rengaraj, K.-H. Yeon, S.-Y. Kang, J.-U. Lee, K.-W. Kim and S.-H. Moon, *J. Hazard. Mater.*, **92**, 185 (2002).
- S. Rengaraj, C.K. Joo, Y. Kim and J. Yi, *J. Hazard. Mater.*, **102**, 257 (2003).
- D. Petruzzelli, R. Passino and G. Tiravanti, *Ind. Eng. Chem. Res.*, **34**, 2612 (1995).
- M.J. DeMarco, A.K. Sen Gupta and J.E. Greenleaf, *Water Res.*, **37**, 164 (2003).
- L. Dong, Z. Zhu, H. Ma, Y. Qiu and J. Zhao, *J. Environ. Sci. (China)*, **22**, 225 (2010).
- B. Pan, H. Qiu, B. Pan, G. Nie, L. Xiao, L. Lv, W. Zhang, Q. Zhang and S. Zheng, *Water Res.*, **44**, 815 (2010).
- Z.-Zhu, H.-Ma, R.-Zhang, Y.-Ge and J.-Zhao, *J. Environ. Sci. (China)*, **19**, 652 (2007).
- L.M. Blaney, S. Cinar and A.K. Sen Gupta, *Water Res.*, **41**, 1603 (2007).
- L. Cumbal and A.K. Sen Gupta, *Environ. Sci. Technol.*, **39**, 6508 (2005).
- S. Sarkar, P.K. Chatterjee, L.H. Cumbal and A.K. Sen Gupta, *Chem. Eng. J.*, **166**, 923 (2011).
- Q.J. Zhang, B.C. Pan, X.Q. Chen, W.M. Zhang, B.J. Pan, Q.X. Zhang, L. Lv and X.S. Zhao, *Sci. Chin. Ser. B*, **51**, 379 (2008).
- S. Mustafa, T. Ahmad, A. Naeem, K.H. Shah and M. Waseem, *Water Air Soil Pollut.*, **210**, 43 (2010).
- D. Petruzzelli, M. Santori, R. Passino and G. Tiravanti, *Water Sci. Technol.*, **30**, 225 (1994).
- S. Mustafa, M.I. Zaman, R. Gul and S. Khan, *Sep. Purif. Technol.*, **59**, 108 (2008).
- D.G. Kinniburgh, J.K. Syers and M.L. Jackson, *Soil Sci. Soc. Am. Proc.*, **39**, 464 (1975).
- M.A. Awan, M.A. Baig, J. Iqbal, M.R. Aslam and N. Ijaz, *J. Appl. Sci. Environ. Manage.*, **7**, 5 (2003).
- M. Kosmulski, *J. Colloid Interf. Sci.*, **353**, 1 (2011).
- M.K. Jha, N. Van Nguyen, J.-Lee, J. Jeong and J.-M. Yoo, *J. Hazard. Mater.*, **164**, 948 (2009).
- Y.-Li, C.-Liu and C.-Chiou, *J. Colloid Interf. Sci.*, **273**, 95 (2004).
- D. Mohan and C.U. Pittman Jr., *J. Hazard. Mater.*, **137**, 762 (2006).
- D.M. Sherman, *Rev. Mineral. Geochem.*, **70**, 181 (2009).
- L. Cumbal, J. Greenleaf, D. Leun and A.K. Sen Gupta, *React. Funct. Polym.*, **54**, 167 (2003).
- A.J. Metson, *N.Z.J. Agric. Res.*, **22**, 95 (1979).
- S.B. Kanungo, S.S. Tripathy, S.K. Mishra, B.R. Sahoo and Rajeev, *J. Colloid Interf. Sci.*, **269**, 11 (2004).
- S. Mustafa, S. Khan, M.I. Zaman and S.Y. Husain, *Appl. Surf. Sci.*, **255**, 8722 (2009).
- M.I. Zaman, S. Mustafa, S. Khan and B. Xing, *J. Colloid Interf. Sci.*, **330**, 9 (2009).
- J. Bajpai, R. Shrivastava and A.K. Bajpai, *Colloids Surf. A*, **236**, 81 (2004).
- D. Mohan, K.P. Singh and V.K. Singh, *J. Hazard. Mater.*, **135**, 280 (2006).
- S.I. Lyubchik, A.I. Lyubchik, O.L. Galushko, L.P. Tikhonova, J. Vital, I.M. Fonseca and S.B. Lyubchik, *Colloids Surf. A*, **242**, 151 (2004).
- T.S. Anirudhan and P.G. Radhakrishnan, *J. Chem. Thermodyn.*, **40**, 702 (2008).
- S. Mustafa, S. Khan and M. Iqbal Zaman, *Water Res.*, **44**, 918 (2010).
- M.L. Machevsky and M.A. Anderson, *Langmuir*, **2**, 583 (1986).