Environ Sci Pollut Res (2017) 24:22353–22360
DOI 10.1007/s11356-017-9823-6

RESEARCH ARTICLE

New hybrid nanocomposite of copper terephthalate MOF-graphene oxide: synthesis, characterization and application as adsorbents for toxic metal ion removal from Sungun acid mine drainage

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Received: 9 March 2017 / Accepted: 24 July 2017 / Published online: 11 August 2017

Abstract The application of a hybrid Cu(tpa).GO (Cu(tpa) copper terephthalate metal organic framework, GO graphene oxide) composite as a new adsorbent for the removal of toxic metal ions was reported. New hybrid nanocomposite with excellent dispersibility and stability was successfully fabricated by the simple and effective ultrasonication method. The synthesized composite was characterized by scanning electron microscopy (SEM), UV-Vis and Fourier-transform infrared (FT-IR) techniques. The characterization results concluded that the binding mechanism of the Cu(tpa) and GO was related to both π–π packing and hydrogen bonding. For scrutinizing the sorption activity, the prepared adsorbents were assessed for the removal of Mn^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and Fe^{3+} metal ions from aqueous synthetic solution and also acid mine drainage (AMD) wastewater. The sorption experiments demonstrated that the removal efficiency was significantly improved by modified hybrid Cu(tpa).GO composite, owing to the significant number of active binding sites and unique structure formed based on π-conjugated networks. Also, it was shown that the adsorption reaction was mainly attributed to the chemical interactions between metal ions and the surface functional groups. Moreover, kinetic and adsorption studies clarified that the adsorption process onto the Cu(tpa).GO follows a pseudo-second-order kinetics and fits the Langmuir and Freundlich adsorption models. Holistically, the results of this research represent that applying Cu(tpa).GO can be remarked as an effective adsorbent with high possibility at conventional water treatment.

Keywords Graphene oxide · Metal organic frameworks · Conjugated nanocomposite · Sorption process · Acid mine drainage · Environmental remediation

Introduction

The most important factor of a healthy life is the dependable water resources free of dangerous and toxic contaminants. Toxic metal ions are counted as one of the waste products of manufacturing processes contaminating water over three centuries of industrialization (Fu and Wang 2011). Acid mine drainage (AMD) composed of toxic metal ions is an emergent pollutant; the development and finding of novel materials for their efficient removal is thus of great significance in the environmental fields. Recently, the formation of AMD as highly contaminated liquid wastes and the release of the dissolved toxic metal ions into the environment are more important concerns for the mining industry. AMD poses a serious threat to human health, animals and ecological systems, resulting from the pyrite oxidation process and the drainage water contains toxic metal ion contaminants (Cu^{2+}, Fe^{3+}, Mn^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}). Some of these metal ions are known to be harmful, carcinogenic and non-biodegradable but tend to be accumulated in the living organisms, causing different kinds of diseases and disorders (Simate and Ndlovu 2014; Kalin et al. 2006; Barrie and Hallberg 2005). There are some conventional techniques which can remove metal ions from water and sewage like oxidation, reduction, chemical

Responsible editor: Guilherme L. Dotto

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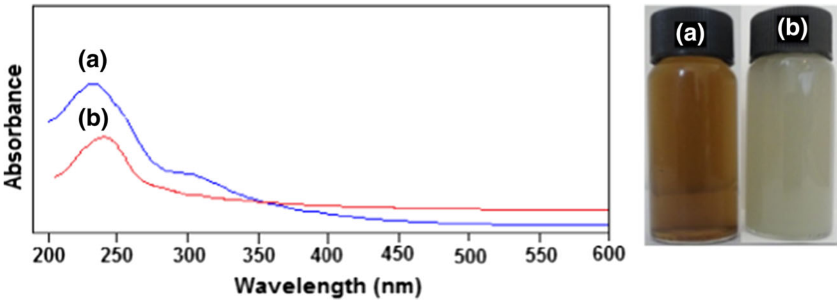


Fig. 1 UV-Vis absorption spectra of GO (**a**) and Cu(tpa).GO (**b**) in water

precipitation, vacuum evaporation, ultra-filtration, ion exchange and adsorption (Klimkova et al. 2011; Mayer et al. 2006; Gomes et al. 2017). Among these, adsorption is especially an interesting method, because it is particularly simple, economical and effective. Several adsorbents such as dairy manure compost (Zhang 2011), bio-carbons (Shin et al. 2008), natural zeolites (Motsi et al. 2009), activated carbon (Kobya et al. 2005) and lignin (Guo et al. 2008) have been reported in AMD treatment. But, the mentioned adsorbents suffer from either low sorption efficiencies or other inefficiencies.

Applying nanotechnology is considered as one of the most important solutions solving the problem of common refining methods. New findings specify that nanoparticles have an influential role removing metal ions from aquatic solutions according to the high surface area, enhanced active sites, crystalline shape, unique network arrangement, abundant functional groups on the surface and high reactivity (Giraldo et al. 2013; Akhbarizadeh et al. 2014; Pradeep and Anshup 2009; Ruparelia et al. 2008; Wang et al. 2010). Within recent years, surface adsorption conducted by highly reactive nanoadsorbents was identified as a technology coped with the environment. Compared with conventional adsorbents, novel researches determine that metal organic frameworks (MOF) and graphene nanosheets have an efficient role removing and decomposing different kinds of organic and inorganic pollutants from the large quantities of aquatic solutions according to the high adsorption capacity and their selectivity (Zhang et al. 2016; Zhao et al. 2011; Yang et al. 2010; Petit and Bandosz 2010; Hasan et al. 2012; Huang et al. 2011; Abedin Khan et al. 2013; Rahimi and Mohaghegh 2016).

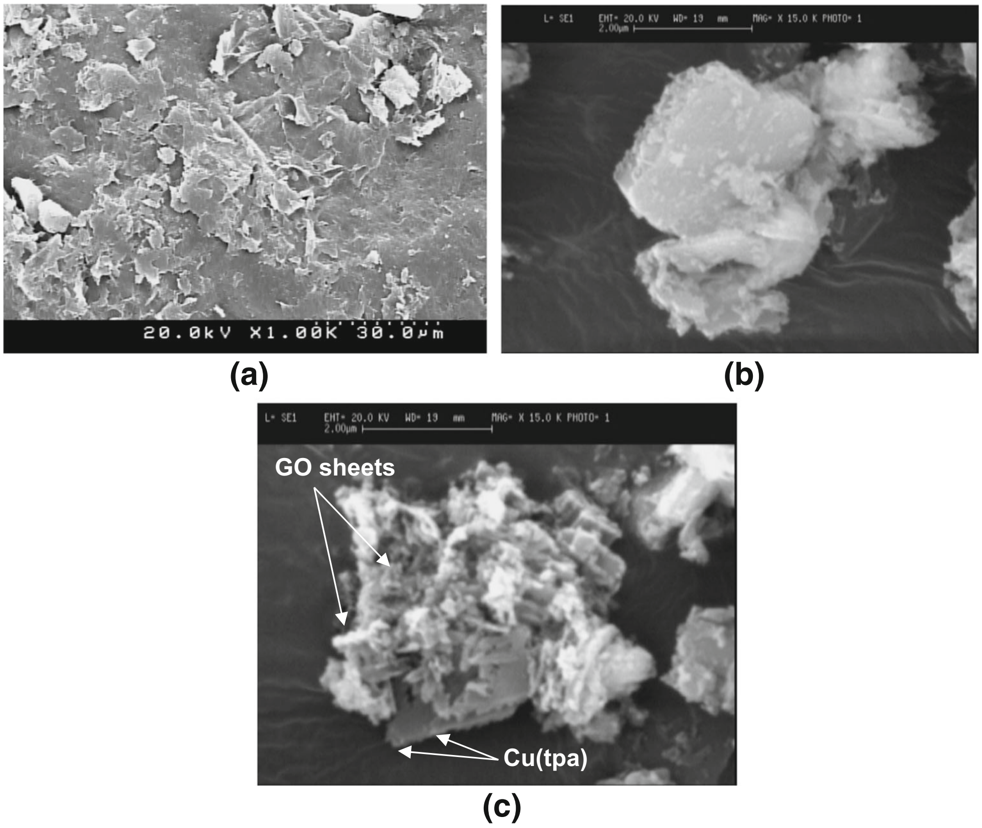


Fig. 2 SEM images of GO (**a**), Cu(tpa) (**b**) and Cu(tpa).GO (**c**) adsorbents

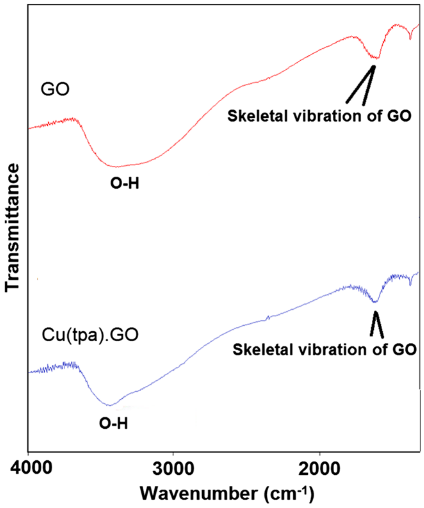


Fig. 3 FT-IR spectra of pure GO and Cu(tpa).GO nanoadsorbents

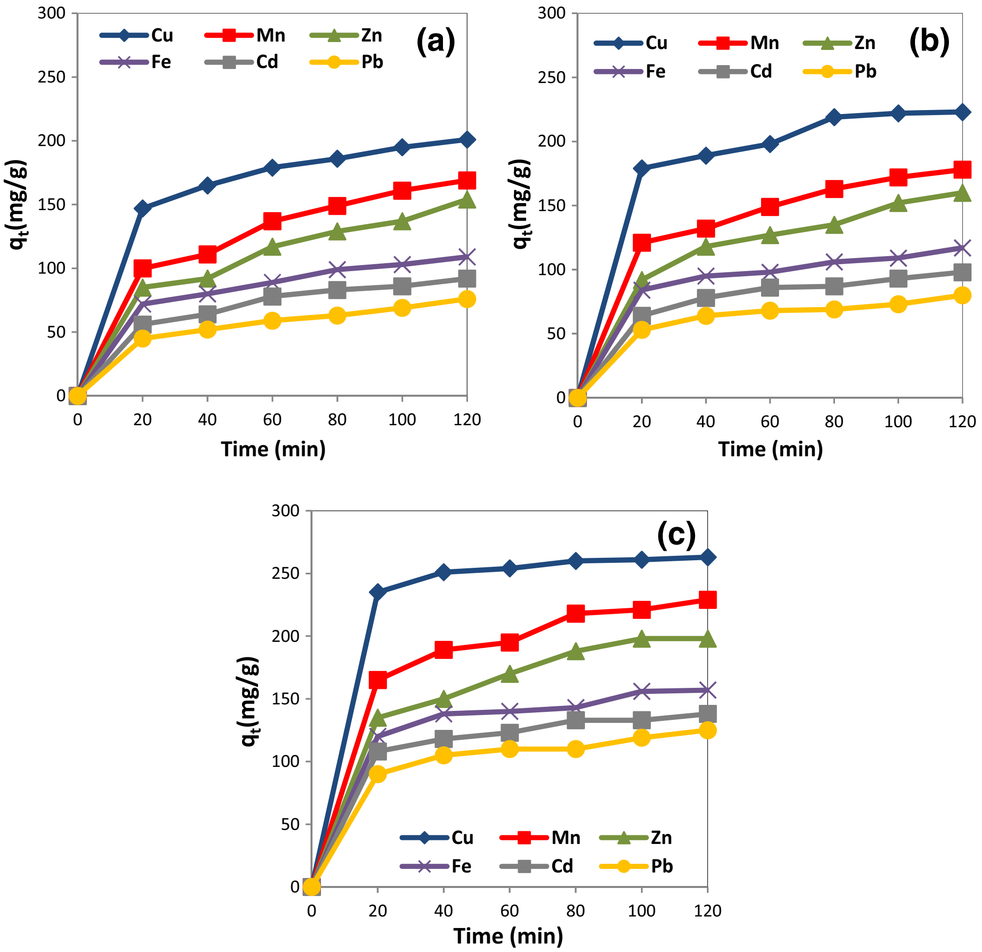
In the current study, the sorption characteristics and removal efficiency of Cu^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and Fe^{3+} metal ions from aqueous solutions similar to AMD from Sungun Copper Mine using new hybrid nanocomposite of copper terephthalate MOF-graphene oxide (Cu(tpa).GO) were studied and also compared with those of pure MOF and GO. The property combination of MOF with GO containing active functional groups via simple sonication method is undoubtedly of special interest in this work. The composite nanoadsorbents were characterized by several techniques. The mechanism of metal ion sorption, sorption kinetic and isotherms is also discussed. Experiments on determining how well the fabricated nanoadsorbents works were performed using both synthetic solution and AMD wastewater of Sungun Copper Mine as a real sample.

Experimental

Instruments

The absorption spectrum of pure GO and Cu(tpa).GO was studied via UV-Vis spectrophotometer (GBC Cintra 40). Morphological properties were examined by SEM (XL30 model). The FT-IR spectra were reported using the ABB

Fig. 4 Removal efficacy of metal ions from synthetic solution with GO (**a**), Cu(tpa) (**b**) and Cu(tpa).GO (**c**) nanocomposite (pH = 7, contact time = 120 min, *T* = 25 °C)



BOMER MB series spectrophotometer. Metal ion concentrations in treated solution containing metal ions were detected via atomic absorption spectrophotometry (AAS) (Varian Spectr AA 220 spectrometer).

Cu(tpa).GO nanoadsorbent fabrication

Copper terephthalate MOF and few-layered GO were fabricated via solvothermal and Hummers' method according to our previous reports, respectively (Rahimi and Mohaghegh 2016; Mohaghegh et al. 2015). Subsequently, the hybrid nanocomposite was synthesized with mixing 1 mg of Cu(tpa) with the aqueous solution of GO (1 mg mL^{-1}) under vigorous stirring, followed by sonication treatment for 2 h to obtain a light blue homogeneous dispersion.

Sorption experiments

A batch reactor surrounded by the circulating water jacket for keeping a temperature constant at about 25 °C was used for the sorption experimental analysis. The reactor was firstly filled with the synthesized solution polluted with metal ions and then adsorbents were fed into the reactor. All metal salts and other chemicals were obtained from Merck. The suspension was magnetically stirred for 120 min at 1000 rpm. At any time intervals, 4 mL of solution was taken out, centrifuged and submitted for AAS analysis.

Results and discussion

UV-Vis absorption spectra of GO and Cu(tpa).GO

The aqueous solution of GO (curve a) and Cu(tpa).GO (curve b) adsorbents was studied by UV-Vis spectroscopy for probing the binding mechanism of GO and Cu(tpa). For curve a, the broad absorption band around 230 nm and a weak shoulder at 290–300 nm related to the π–π* transitions of unoxidized aromatic C=C and *n*–π* transition of the C=O, respectively (Fig. 1a) (Mohaghegh et al. 2015). As represented in Fig. 1b, the absorption peak of GO around 230 nm is red-shifted to 240 nm. It demonstrates that the electronic conjugation within GO has been stored after interaction with Cu(tpa) (Mohaghegh et al. 2015). Therefore, the main reason for the hybrid composite fabrication can be related to the π electrons conjugation between terephthalate linker in MOF and the unoxidized aromatic rings. For curve b, the weak shoulder of GO completely disappeared for Cu(tpa).GO. This observation shows that two species might also interact through hydrogen bonding and/or Cu−O coordination bond based on the UV-Vis absorption spectra (Wang et al. 2014). Interestingly, the absorption spectrum of stored Cu(tpa).GO was hardly changed after 1 month. So, Cu(tpa).GO as an adsorbent has excellent chemical stability. Besides, colour change of GO solution also confirms the interactions between Cu(tpa) and GO.

SEM

The morphological properties of the as-prepared nanoadsorbents were characterized by FE-SEM images (Fig. 4). Figure 2a clearly shows that the GO adsorbent consists of randomly aggregated thin sheets gathered with each other. As indicated in Fig. 2b, the Cu(tpa) sample displays a cubic shape with a relatively smooth surface. From the SEM images of Cu(tpa).GO nanocomposite (Fig. 2c), it was found that the GO sheets co-wrapped the cubic-shaped Cu(tpa) sample.

FT-IR spectroscopy

For studying the GO and terephthalate interaction mechanism in Cu(tpa).GO, FT-IR spectroscopy was used (Fig. 3). The bands appearing around 3386 and 1620 cm^{-1} are related to the O−H and skeletal vibration of unoxidized graphitic domains of GO sheets, respectively. After interaction with

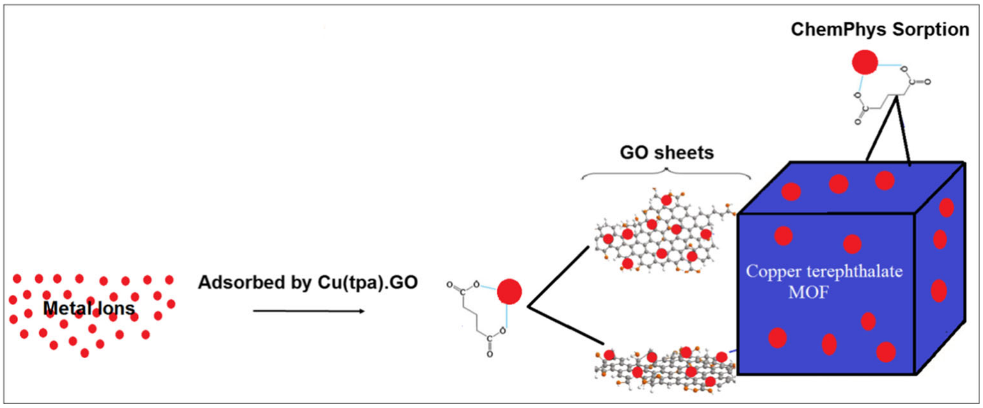


Fig. 5 The structures of Cu(tpa).GO-conjugated composite with attached metal ions

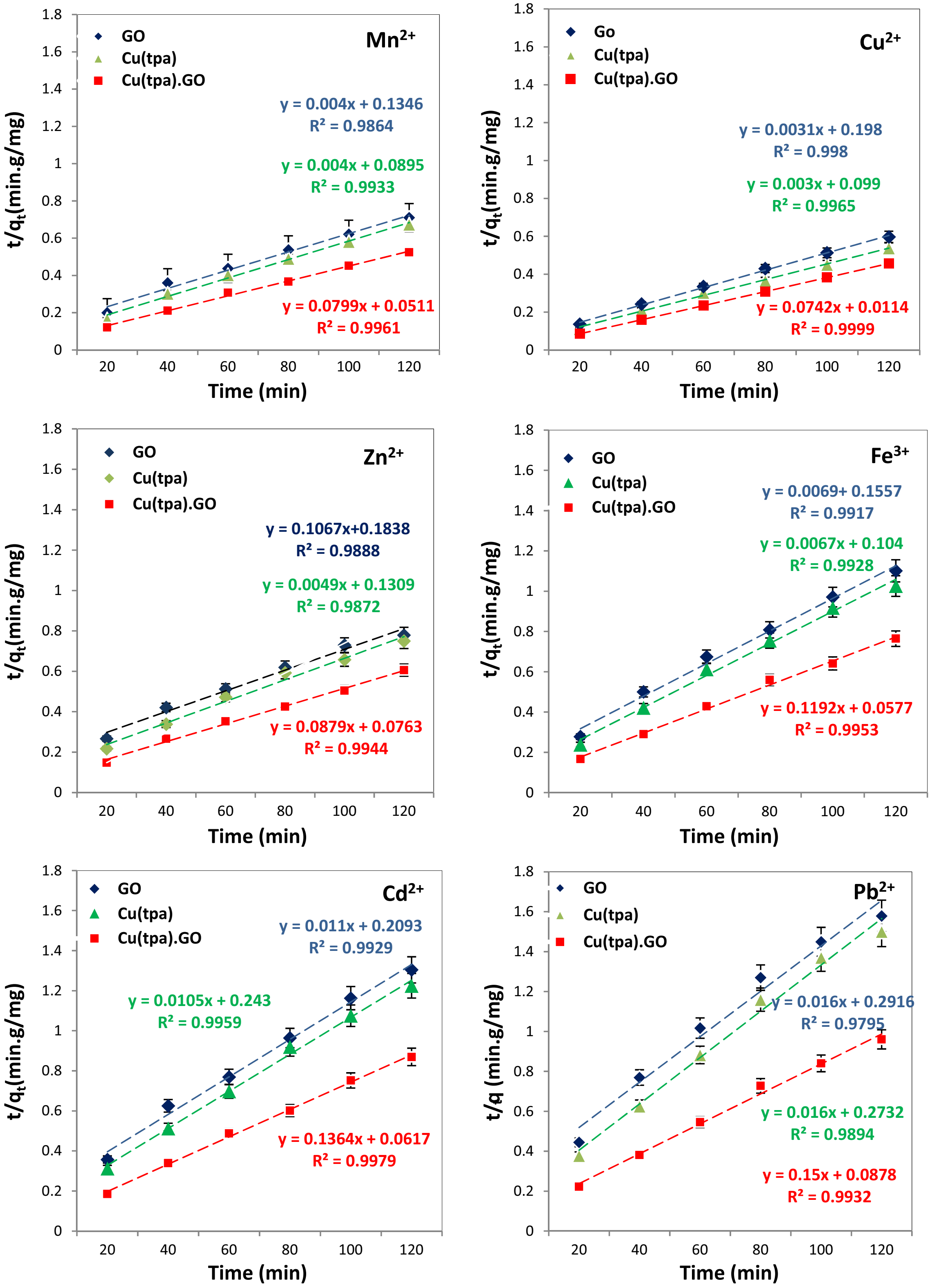


Fig. 6 Pseudo-second-order kinetic curves for ion sorption onto all prepared nanoadsorbents

copper terephthalate MOF, the peak assigned to the skeletal vibration of the GO shifted to 1635 cm^{-1} (Wang et al. 2014). This obviously different behaviour demonstrates that the GO and MOF interactions in GO-based composite are π–π packing and hydrogen bonding same as the UV-Vis spectroscopy conclusions. The strong band of OH

Table 1 Mathematical equations applied in adsorption isotherm study of metal ions onto Cu(tpa).GO nanocomposite

Models	Linear eq.	Plot	Calculated coefficient
Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_f}$	$\frac{C_e}{q_e}$vs C_e	$K_L = \frac{Slope}{Intercept}$ $q_m = Slope^{-1}$
Freundlich	$\log q_e = \log K_F + \frac{logC_e}{n}$	Log $q_e$vs log C_e	$K_F = 10^{Intercept}$ $n = Slope^{-1}$

proposes a great number of these groups existing on the GO-based adsorbent surface that plays an influential role in toxic metal ion removal.

Sorption of metal ions over prepared adsorbents

The sorption efficacy results over nanoadsorbents are illustrated in Fig. 4. q_t is the amount of metal ions adsorbed at time t (mg g^{-1} adsorbent). Cu(tpa).GO showed the highest efficacy for total metal ion removals. Some reasons may be explained for the clarification of the highest sorption efficiency over the Cu(tpa).GO. (i) The great number of active sites existed on the Cu(tpa).GO hybrid composite spontaneously tends to adsorb metal ion. Metal ions were chemically sorbed via inclosing the metal ions with some special groups such as epoxides, hydroxides, carboxylic groups and carboxylate existed on the surface of Cu(tpa).GO as the most active adsorbent. (ii) Metal ions can be adsorbed over GO by collecting ions along the wrinkles and edges of it. (iii) The porous structure of new hybrid composite enables metal ions to easily diffuse into the MOF.

According to our previous paper, adsorption is a heterogeneous reaction remarking an initial fast adsorption step followed by one at a slower rate for pure GO and copper terephthalate MOF (Rahimi and Mohaghegh 2016). This study also confirmed gained results for new Cu(tpa).GO nanocomposite adsorbents. This is mainly because of the initially more available active sites and easy interaction of them with ions. This first step of the fast adsorption ascribes to the ion exchange into the pores and also adsorption on the sorbent surface. Additionally, the initially very high concentration difference between bulk solution and solid/liquid interface (as a driving force) causes to the improved adsorption rate. However, the slower adsorption may be owing to the slower diffusion of metal ions into the available pores of adsorbents. The mechanism for total metal ion removal over the hybrid Cu(tpa).GO adsorbent is schematically represented in Fig. 5.

Kinetic adsorption study of metal ions on conjugated nanocomposite

The quantitative kinetic order and adsorption rate constant for the metal ion removal via adsorption were evaluated (Fig. 6). The pseudo-second-order rate equations were used for investigating the adsorption mechanism and kinetics and fitted well for all metal ions. This kinetics model is consistent with the assumption that the determining rate step may be chemical sorption consisting of valence forces formed via electronic interaction between the adsorbent and the adsorbate samples (Rahimi and Mohaghegh 2016; Ríos et al. 2008). The pseudo-second-order chemisorption kinetics model is represented according to Eq. 1:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{1}$$

Separating the variables in Eq. 1 expresses (Eq. 2):

$$\frac{dq_t}{(q_e - q_t)^2} = kdt \tag{2}$$

Table 2 Isotherm parameters of metal ion adsorption on Cu(tpa).GO as a conjugated adsorbent

Metal	Langmuir model			Freundlich model		
	q_m	K_L	R^2	$\frac{1}{n}$	K_F	R^2
Pb(II)	88	6.0×10^{-3}	0.996	0.47	3.5	0.932
Cu(II)	243	1.9×10^{-3}	0.988	0.26	45.1	0.945
Zn(II)	131	2.3×10^{-3}	0.977	0.63	1.4	0.995

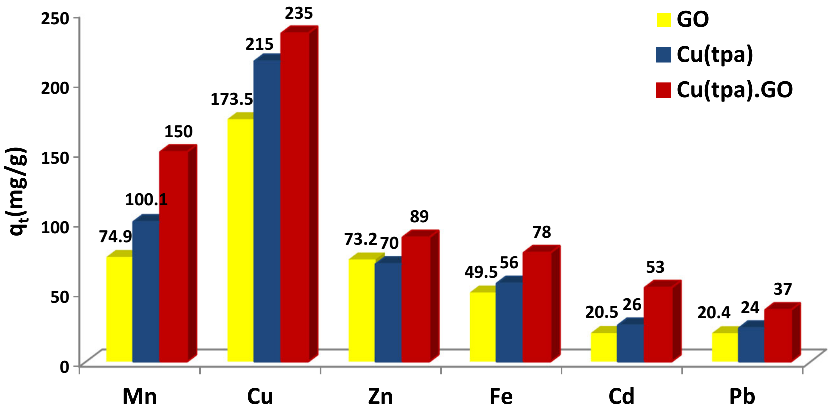


Fig. 7 Comparison of AMD removal efficacy among used nanosorbents (contact time = 120 min, $T = 25$ °C)

In which, q_e is the amount of adsorbed per unit mass at equilibrium, q_t is the amount of metal ions adsorbed at time t (mg g^{-1} adsorbent) and k is the second-order rate constant (g mg^{-1} min^{-1}). A linear form of the typical second-order rate equation is shown as (Eq. 3):

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \tag{3}$$

And h can be estimated from Eq. 4.

$$h = kq_e^2 \tag{4}$$

The pseudo-second-order model constants can be calculated via plotting $\frac{t}{q_t}$ versus time (t). Kinetic sorption curves of metal ions on the used sorbents are shown in Fig. 6.

Sorption isotherms

Explained equations accurately provide more results demonstrated in this study and it is believed that they can be greatly utilized for analysing the isotherm data. Langmuir and Freundlich adsorption isotherms are the main isotherms for analysing of adsorption isotherms (Rahimi and Mohaghegh 2016; R’ıos et al. 2008). These models are considered by the authors to be the best available for describing sorption of metal ions onto the conjugated composite. Mathematical equations applied in Langmuir and Freundlich adsorption isotherm study of toxic metal ions over hybrid Cu(tpa).GO nanocomposite are illustrated in Table 1.

In which, C_e is the metal ion concentration (mg L^{-1}) at equilibrium; q_e is the amount of metal ions adsorbed per gramme of adsorbent at equilibrium (mg g^{-1} adsorbent).

In this study, the sorption data for Cu^{2+}, Zn^{2+} and Pb^{2+} with Cu(tpa).GO adsorbent were fitted into both linearized Langmuir and Freundlich model and the obtained results are represented in Table 2.

Removal of toxic metal ions from natural AMD

In order to further study how conjugated Cu(tpa).GO works as an adsorbent, AMD wastewater of Sungun Copper Mine was tested as a real sample and the results are reported in Fig. 7. AMD wastewater was collected from the low-grade sulphur deposit in Sungun Copper Mine. For the real sample, 1000 mL of AMD sample including metal ions and 0.1 g of adsorbents was fed into the reactor. The concentrations of Cu^{+2}, Mn^{+2}, Cd^{+2}, Zn^{+2}, Fe^{3+} and Pb^{+2} ions in AMD sample were 228.1, 112.4, 35.9, 91.7, 73.7 and 35.1 mg/L, respectively. So, the concentrations of metal ions in this case study are high that pollutes the mine environment. New hybrid Cu(tpa).GO nanocomposite showed the highest total removal efficiency.

Conclusion

A new hybrid Cu(tpa).GO nanocomposite was successfully fabricated and characterized. The adsorption behaviour of the new Cu(tpa).GO adsorbent has been studied for the metal ion removal. The Cu(tpa).GO provides an efficient, fast and environmentally friendly approach for the removal of metal ions from both aqueous synthetic solutions and AMD wastewater of Sungun Copper Mine as a case study. The results demonstrated that the special characteristics of hybrid sorbent such as the unique structure formed by π-conjugated networks, binding capacity and specific functional groups as binding sites considerably influence and enhance the uptake efficiency. The suggested mechanism for the metal ion removal by hybrid nanocomposite is greatly in agreement with the Langmuir and Freundlich adsorption isotherms. Also, the sorption kinetics data confirmed that the sorption reaction obeys the pseudo-second-order kinetics. Interestingly, ion removal results from real sample of mine-related AMD (from Sungun Copper Mine) shows that Cu(tpa).GO have great potential as an adsorbent for the preconcentration of metal ions.

References

Abedin Khan N, Hasan Z, Hwa Jhung S (2013) Adsorptive removal of hazardous materials using metal-organic frameworks (MOFs): a review. J Hazard Mater 244-245:444–456

Akhbarizadeh R, Shayestefar MR, Darezereshki E (2014) Competitive removal of metals from wastewater by maghemite nanoparticles: a comparison between simulated wastewater and AMD. Mine Water Environ 33:89–96

Barrie JD, Hallberg KB (2005) Acid mine drainage remediation options: a review. Sci Total Environ 338:3–14

Fu F, Wang Q (2011) Removal of heavy metal ions from wastewaters: a review. J Environ Manag 92:407–418

Giraldo L, Erto A, Moreno-Piraján JC (2013) Magnetite nanoparticles for removal of heavy metals from aqueous solutions: synthesis and characterization. Adsorption 19:465–474

Gomes HI, Jones A, Rogerson M, Greenway GM, Fernandez Lisbona D, Burke IT, Mayes WM (2017) Removal and recovery of vanadium from alkaline steel slag leachates with anion exchange resins. J Environ Manag 187:384–392

Guo X, Zhang S, Xq S (2008) Adsorption of metal ions on lignin. J Hazard Mater 151:134–142

Hasan Z, Jeon J, Jhung SH (2012) Adsorptive removal of naproxen and clofibric acid from water using metal-organic frameworks. J Hazard Mater 209-210:151–157

Huang CY, Song M, Gu ZY, Wang HF, Yan XP (2011) Probing the adsorption characteristic of metal-organic framework MIL-101 for volatile organic compounds by quartz crystal microbalance. Environ Sci Technol 45:4490–4496

Kalin M, Fyson A, Wheeler WN (2006) The chemistry of conventional and alternative treatment systems for the neutralization of acid mine drainage. Sci Total Environ 366:395–408

Klimkova S, Cernik M, Lacinova L, Filip J, Jancik D, Zboril R (2011) Zero-valent iron nanoparticles in treatment of acid mine water from in situ uranium leaching. Chemosphere 82:1178–1184

Kobya M, Demirbas E, Senturk E, Ince M (2005) Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. Bioresour Technol 96:1518–1521

Mayer KU, Benner SG, Blowes DW (2006) Process-based reactive transport modeling of a permeable reactive barrier for the treatment of mine drainage. J Contam Hydrol 85:195–211

Mohaghegh N, Tasviri M, Rahimi E, Gholami MR (2015) A novel p–n junction $Ag_3PO_4/BiPO_4$ based stabilized Pickering emulsions for highly efficient photocatalysis. RSC Adv 5:12944–12955

Motsi T, Rowson NA, Simmons MJH (2009) Adsorption of heavy metals from acid mine drainage by natural zeolite. Int J Miner Process 92:42–48

Petit C, Bandosz TJ (2010) Enhanced adsorption of ammonia on metal-organic framework/graphite oxide composites: analysis of surface interactions. Adv Funct Mater 20:111–118

Pradeep T, Anshup (2009) Noble metal nanoparticles for water purification: a critical review. Thin Solid Films 517:6441–6478

Rahimi E, Mohaghegh N (2016) Removal of toxic metal ions from Sungun acid rock drainage using mordenite zeolite, graphene nanosheets, and a novel metal–organic framework. Mine Water Environ 35:18–28

Ríos CA, Williams CD, Roberts CL (2008) Removal of heavy metals from acid mine drainage (AMD) using coal fly ash, natural clinker and synthetic zeolites. J Hazard Mater 156:23–35

Ruparelia JP, Duttagupta SP, Chatterjee AK, Mukherji S (2008) Potential of carbon nanomaterials for removal of heavy metals from water. Desalination 232:145–156

Shin EJ, Lauve A, Carey M, Bukovsky E, Ranville JF, Evans RJ, Herring AM (2008) The development of bio-carbon adsorbents from Lodgepole Pine to remediate acid mine drainage in the Rocky Mountains. Biomass Bioenergy 32:267–276

Simate GS, Ndlovu S (2014) Acid mine drainage: challenges and opportunities. J Chem Eng Environ 2:1785–1803

Wang J, Zheng S, Shao Y, Liu J, Xu Z, Zhu D (2010) Amino-functionalized $Fe_3O_4@SiO_2$ core–shell magnetic nanomaterial as a novel adsorbent for aqueous heavy metals removal. J Colloid Interface Sci 349:293–299

Wang X, Wang Q, Wang Q, Gao F, Yang Y, Guo H (2014) Highly dispersible and stable copper terephthalate metal−organic framework−graphene oxide nanocomposite for an electrochemical sensing application. ACS Appl Mater Interfaces 6:11573–11580

Yang STY, Chang L, Wang HF, Liu GB, Chen S, Wang YW, Liu YF, Cao AN (2010) Folding/aggregation of graphene oxide and its application in Cu^{2+} removal. J Colloid Interface Sci 351:122–127

Zhang M (2011) Adsorption study of Pb(II), Cu(II) and Zn(II) from simulated acid mine drainage using dairy manure compost. Chem Eng J 172:361–368

Zhang Y, Jiao Z, Hu Y, Lv S, Fan H, Zeng Y, Hu J, Wang M (2016) Removal of tetracycline and oxytetracycline from water by magnetic Fe_3O_4@graphene. Environ Sci Pollut Res:1–9

Zhao G, Ren X, Gao X, Tan X, Li J, Chen C, Huang Y, Wang X (2011) Removal of Pb(II) ions from aqueous solutions on few-layered graphene oxide nanosheets. Dalton Trans 40:10945–10952