

Development of PANI/BN-based absorbents for water remediation

Muhammad Arsalan, Azka Awais, Tingting Chen, Qinglin Sheng and Jianbin Zheng

ABSTRACT

In this research, novel PANI/BN-based absorbent was prepared by bonding polyaniline and bentonite for water remediation and their structures were characterized by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The effect of pH, concentration of metal, and dosage amount on synthesized novel PANI/BN-based absorbent was investigated in detail. The result indicated that the PANI/BN-based absorbent has an excellent adsorption performance towards Cu, Pb, and Ni, and the highest binding capacity of 130 mg g^{-1} for Ni was obtained under normal conditions. The adsorption of PANI/BN absorbent was found to depend on pH when $\text{pH} < 7.0$, but the adsorption has been found independent from the ionic bond effect. The adsorption at optimum pH for Cu (pH 6) and Pb (pH 5) was observed as 85 mg g^{-1} and 105 mg g^{-1} , respectively. The best results collected at those conditions of isotherm data and adsorption kinetics are represented by the Langmuir model and pseudo-second order equation, respectively. Thermodynamic results ($\Delta H > 0$, $\Delta S > 0$, $\Delta G < 0$) showed that the adsorption process of Cu, Ni, and Pb is significantly increased by the synthesized novel PANI/BN-based absorbent.

Key words | adsorption, bentonite, PANI/BN-based absorbent, thermodynamic, water remediation

Muhammad Arsalan

Azka Awais

Tingting Chen

Qinglin Sheng (corresponding author)

Jianbin Zheng

College of Chemistry and Materials Science/Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education/ Shaanxi Provincial Key Laboratory of Electroanalytical Chemistry, Northwest University, Xi'an, Shaanxi 710069, China
E-mail: qinglinsheng@126.com

Qinglin Sheng

College of Food Science and Technology, Northwest University, Xi'an, Shaanxi 710069, China

INTRODUCTION

Water is essential for all life forms on Earth. Availability of clean water is of immense importance. Water pollution is a worldwide major problem and the main cause of disease and death worldwide. Most water contaminants arise from anthropogenic sources including contaminants, such as fertilizers, detergents, textile dyes, pathogens, herbicides, heavy metals and pesticides, poisonous industrial chemicals that enter into drinking water and render it unsafe for drinking. Heavy metals like Pb, Cd, and Cr are harmful to the human body, which is why they need to be removed from drinking water. Some scientists have used herbs and fungus (*Pleurotus ostreatus*) to remove those heavy metals (Yang *et al.* 2017). Heavy metals encounter fresh water and become a part of it through which they can enter the human body. Some heavy metals are essential in maintaining the digestion process. The human body requires Cu, Zn, Co, and Fe but an

increased amount can cause adverse effects. Metals like Cu in excessive amounts cause serious environmental problems (Zhai *et al.* 2015). Heavy metal pollution in the sediments of different regions depend on dry and wet seasons and can be found with the help of certain techniques. For example, in the Pra Basin of Ghana, metals like Cr, Pb, Cd, and Ni are enriched in the wet season but in the dry season enrichment of Pb and Cr was observed due to human activities which cause water pollution (Duncan *et al.* 2018). Most heavy metals are toxic even if present in trace amounts and become a cause of environmental pollution due to their non-degradable, persistent, and accumulative nature (Gupta & Ali 2004). The EPA (Environmental Protection Agency) compiled studies about how the underground water becomes polluted and four factors were identified as culprits for this purpose. These are heavy metals, chlorides, nitrates, and

hydrocarbons. The concentrations of Cd, Cr, Ni, and Pb were higher than their respective permissible limits, while Cu, Mn, and Zn concentrations were observed to be within their respective limits. Health risk indicators, such as chronic daily intake (CDI) and the health risk index (HRI), were calculated for adults and children separately and identified hazardous water effects on their health (Khan *et al.* 2013). Due to possible health issues caused by heavy metals, researchers are focusing on understanding the metal reactions in the environment. Man's activities are constantly disturbing the environment by introducing heavy metals like Cd(II) into terrestrial and aquatic ecosystems (Xiong *et al.* 2009). Since its first introduction for heavy metal removal, activated carbon has undoubtedly been the most popular and widely used adsorbent in wastewater treatment applications throughout the world. However, activated carbon is very expensive and its performance can be enhanced only with some complexing agent (Meneghel *et al.* 2014). Alternatively, research is being undertaken to discover a cost-effective adsorbent. Chitosan and natural zeolite has attracted considerable attention due to the low cost and remarkable metal binding activities (Wang *et al.* 2012). These compounds are being used as adsorbents for metal. Clay is one of the potential alternatives to activated carbon as well as some other adsorbents like chemically synthesized alkyl-substituted sPANIs/Ch-HCl (polyaniline/chitosan) composites which were used as potential adsorbent for Cr (Yavuz *et al.* 2011). Like zeolites, clay minerals are also important inorganic components in soil. Clays are one of the most widely used adsorbents. They have large specific surface areas; stabilities (mechanical and chemical) are also high. This research presents a cost-effective and easy method for developing a reliable adsorbent. Bentonite is a phyllosilicate clay containing aluminum. It is widely used as an adsorbent. Mostly montmorillonite is present in it in large amounts. This clay has been given the name 'bentonite' (Hostermen & Patterson 1992). Bentonite and fuller's earth are resources of the United States (Hostermen & Patterson 1992).

MATERIALS AND METHODS

All chemicals of analytical grade were obtained from Sigma Aldrich and used without any purification step. Milli-Q

water was used to make all solutions. All apparatus was used after calibration. A weighing balance (Armfield), pH meter (Hach Sension+), furnace (MHA-11), oven (EYLA-450NDO), filtration apparatus (MDA-015), hot plate (magnetic stirrer hot plate) were used. For characterization of samples, atomic absorption spectrometry (AAS) (Perkin Elmer Analyst 800 Series) and scanning electron microscopy (SEM) (JSM-6480) analysis was conducted.

Methods

Preparation of polyaniline

To prepare the composite first polyaniline was prepared. For this purpose, aniline was first taken (5.0 g) and dissolved in 1 N HCl (250 mL). This mixture was placed in an ice bath and the temperature was kept below 5 °C. In another beaker, 0.3 M precooled ammonium persulfate was placed. Chilled APS (as prepared solution) was dissolved in HCl (1 N). This mixture of APS with HCl was added very slowly into the mixture of aniline. During mixing the solution was continuously stirred. Both solutions were mixed for 30 minutes. This reaction is highly exothermic with $\Delta H = 372$ kJ/mol, so the stirring was done in an ice bath during all oxidation cooling. The reaction vessel was stirred for a further 2 hours after the mixing of the two solutions and oxidation reaction was completed. Again, the temperature was kept below 5 °C. The solution vessel was kept overnight at room temperature in an unstirred condition. The next day the polymer was precipitated out in as a dark blue color. These precipitates were filtered then washed with a large amount of distilled water and with a dilute solution of HCl. Washing was continued until a colorless washing liquid was observed. To get rid of non-polymeric impurities and oligomers, precipitates were washed with methanol and water (distilled). The polyaniline was dried in an oven at 50–60 °C. The powdered polyaniline was obtained by grinding the polyaniline in a pestle and mortar. It was then stored for further processing.

Bentonite source and conditioning

To thermally activate bentonite, its powder was washed with distilled water and then dried at 100–110 °C for 4 hours. It was then passed through a sieve using mesh size 120. Finally,

it was stored for further use. This was the thermal activation of bentonite.

Preparation of polyaniline composite

First, the polyaniline was reacted for 2 hours with 0.5 M NaOH solution to solubilize polyaniline in formic acid. Then, the solution was washed with distilled water and the polyaniline was dried again in an oven at 60 °C. Polyaniline is often referred to as emeraldine base (EB) and 5.0 g of this EB was taken and dissolved in 50 mL of formic acid. Filtration was done to remove any insoluble solid impurities. 5 g of bentonite was taken and added into 25 mL of EB in formic acid. The mixture was stirred for 2 hours in a magnetic stirrer and then left unstirred for another 2 hours.

The PANI/BN composite was subjected to evaporation by placing the mixture in an oven at 60 °C and evaporating the excess solvent. The composite was obtained in powdered form and stored for further use.

Preparation of metal solution

10, 20, 30, 40, and 50 mg/L solutions of Cu, Ni, and Pb were prepared from stock solution.

Batch studies

Removal of copper, lead, and nickel by PANI/BN was studied using a batch approach. For complete examination of adsorption of PANI/BN, 50 mL of stock solution of heavy metals (Ni, Pb, and Cu) was added in the desired amount of chosen adsorbent. The solution was agitated at the desired speed for a specific time at room temperature. The solution was filtered and concentration of heavy metals was found by atomic adsorption spectroscopy.

RESULTS AND DISCUSSION

Scanning electron microscopy was used to study surface topography of PANI/BN, Cu/COM, Ni/COM, and Pb/COM (Figure 1). As shown in Figure 1, before the treatment of metal, the PANI/BN shows a small rough stone-like structure. However, after the adsorption of Cu, Ni, and Pb on PANI/BN

composite, increases in the size of specimens are observed. Figure S1 in the Supplementary Information (available with the online version of this paper) shows the Fourier transform infrared (FTIR) spectra of PANI before and after adsorption of Pb, Cu, and Ni. The characteristic peaks observed in Figure S1 are summarized in Table 1. From Table 1, it can be seen that all bands of the FTIR in the composite have shifted significantly. This shows the interaction between the polyaniline and bentonite. The peak at 3,170 cm^{-1} which corresponds to the =NH stretching band shows a peak at 3,000 in the composite and has shown remarkable changes after the adsorption of metals show peaks at 3,349 cm^{-1} (Cu), 3,361 cm^{-1} (Ni), 3,346 cm^{-1} (Pb). Hence, it can be inferred that the metals' adsorption has been taken place on the =NH bond.

Condition optimization

Influence of pH and agitation speed

The study of pH is one of the most important factors in adsorption studies. This factor not only affects the adsorption process by influencing the binding sites, but also affects the hydrolysis, redox potentials, and complexation formation of metals with ligands (organic/inorganic) in solution. The pH effect was studied in the range of 2–8 at constant agitation speed of 200 rpm for 30 minutes at room temperature. At extremely low pH, due to protonation of active sites of adsorbent, metal species could not be absorbed at all, similarly the above three metals are converted into their hydroxides so pH 6 was selected as the optimum pH value. The pH was adjusted with dilute HCl and using NaOH. Figure 2(a) shows that maximum adsorption of Pb occurred at pH 8 but the literature has shown that in some cases maximum absorption occurs at pH 5 (Mehwish *et al.* 2013). Thus, pH 5 was taken as the optimum pH value for Pb adsorption in the present study. By repeating the process, the average adsorption value for Pb was 105 mg g^{-1} . The average adsorption value at optimum pH 6 for Cu was observed as 85 mg g^{-1} . The maximum adsorption of Ni is found at pH 8. However, considering that precipitation of Ni will take place after 7.4, pH 7 was selected as the optimum having an adsorption value of 130 mg g^{-1} .

Adsorption of Cu, Ni, and Pb on PANI/BN was studied as a function of agitation speed. Experiments were

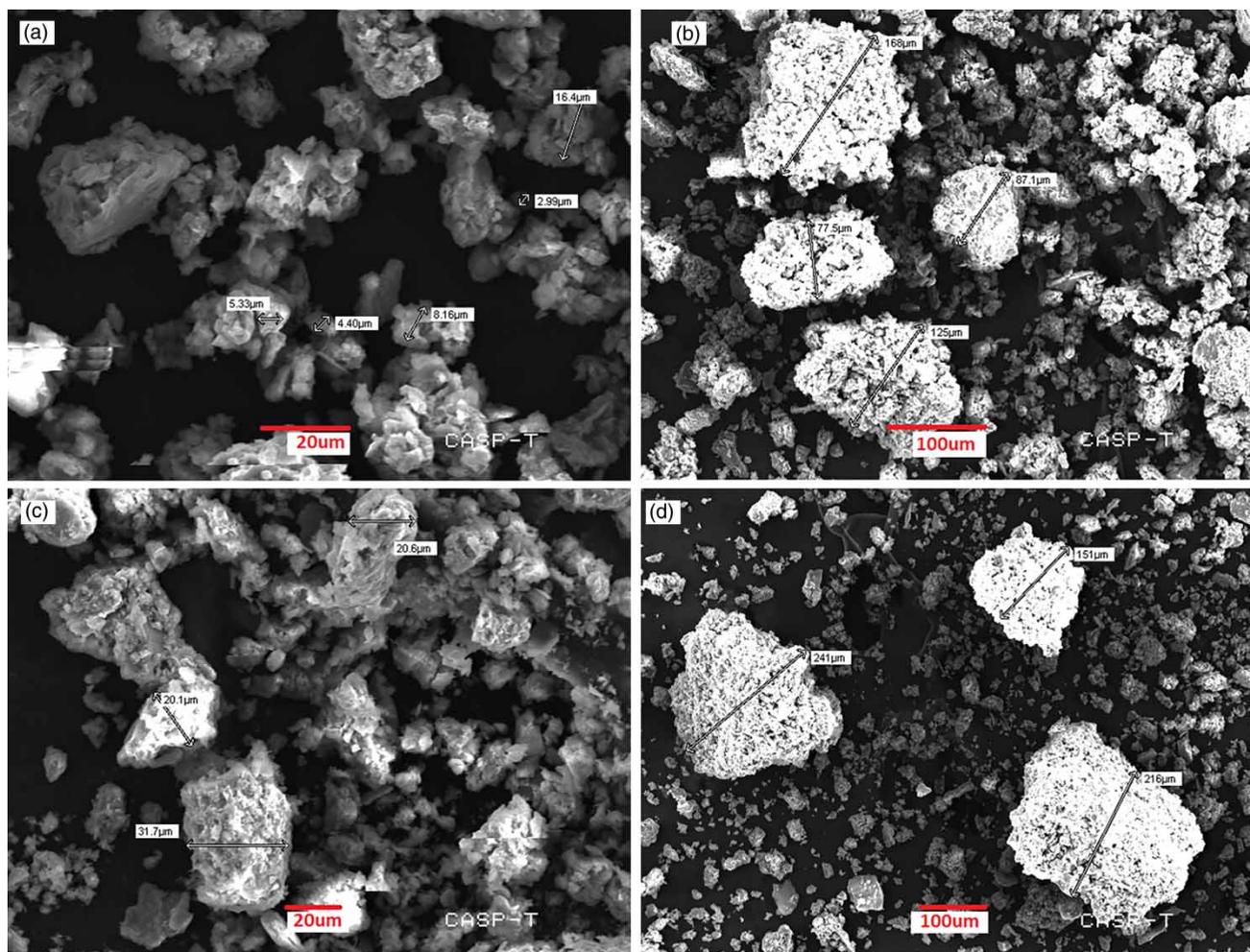


Figure 1 | SEM images of (a) PANI/BN composite, SEM images of (b) Cu, (c) Pb, and (d) Ni adsorbed on PANI/BN.

Table 1 | FTIR peaks of PANI/BN composite before and after Cu, Ni and Pb adsorption

Composite before adsorption cm^{-1}	Composite after adsorption (Cu) cm^{-1}	Composite after adsorption (Ni) cm^{-1}	Composite after adsorption (Pb) cm^{-1}	Assignment
3,000	3,349	3,361	3,346	H bonded NH stretching
1,600	1,639	1,640	1,637	N = quinoid unit = N stretching
1,496	1,500	1,506	1,495	N-benzenoid unit-N stretching
1,305	1,309	1,308	1,310	C-N stretching in quinoid- trans benzenoid unit-quinoid unit
1,141	1,036	1,035	1,036	Mode of quinoid unit = NH-benzenoid unit
829	793	789	793	C-H out of plane 1,4 ring
645	691	688	691	Aromatic deformations
511	525	526	524	Aromatic deformations
408	465	463	463	Aromatic deformations

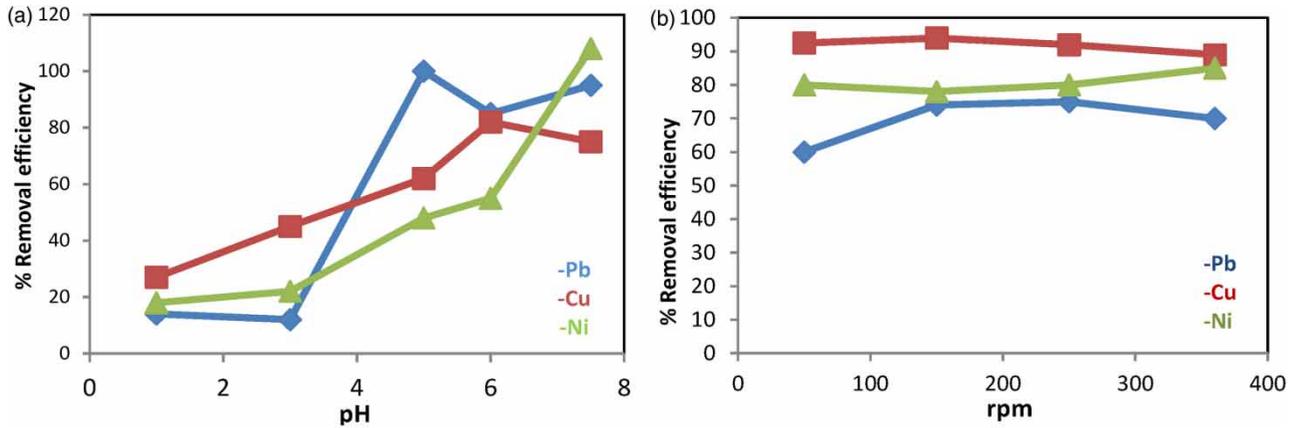


Figure 2 | Percentage removal efficiency of Pb, Cu, and Ni by PANI/BN by varying pH (a) and agitation speed (b).

performed by varying the agitation rate from 50 to 400 rpm. Percentage removal efficiency of each metal is shown in Figure 2(b). Results indicated that for Cu, Ni, and Pb, maximum adsorption occurred at 200, 400, and 200 rpm, respectively. At low rpm adsorbent is not well separated and distributed and accumulates at the bottom thus rendering the active sites of the low layered adsorbent from meeting metal ions. At very high speed, the removal efficiency decreases due to the desorption inclination of metal ions.

Effect of metal concentration and dosage amount

Initial metal concentrations significantly affect batch adsorption performance. To inspect the effect of initial concentrations of Ni, Cu, and Pb on percentage removal

efficiency, experiments were carried out with initial metal concentrations ranging from 10 to 50 mg/L under the optimized conditions of pH, contact time, and dosage mentioned above. Results are shown in Figure 3(a): for Cu the maximum adsorption was seen at 10 mg/L; for Pb the removal efficiency was found to be highest at 10 mg/L, after which it started to decrease by further increase in initial concentrations; for Ni, the increase in initial concentration resulted in a slight and gradual increase in maximum adsorption, which occurred at 50 mg/L. At saturation point, all active sites are occupied so by changing the initial concentration, adsorption remains constant.

Dosage concentration also influences the adsorption process. Results of variation of dosage amount on removal efficiency of Cu, Ni, and Pb are shown in Figure 3(b). As the dose amount increased from 2 to 20 g/L, an increase

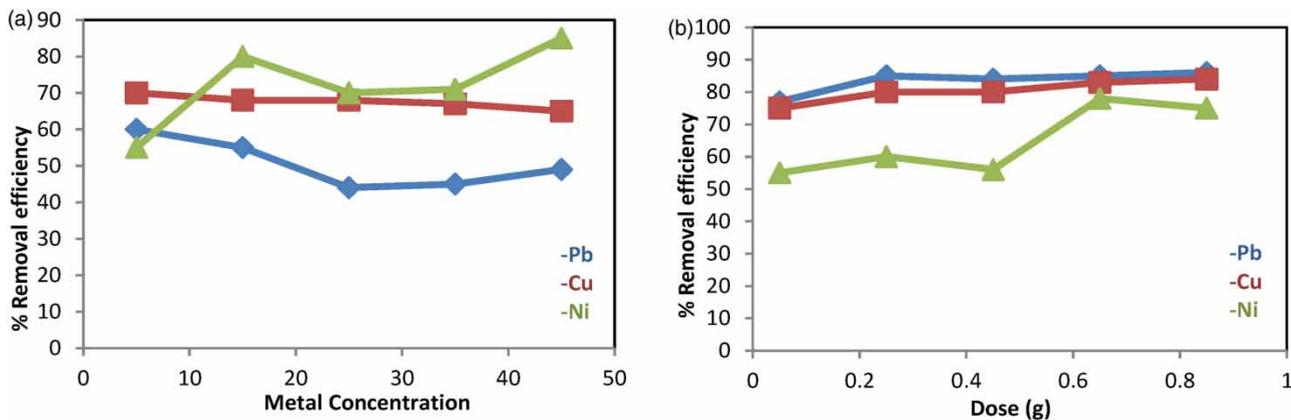


Figure 3 | Influences of metal concentration (a) and dosage amount (b) towards the removal of Pb, Cu, and Ni by PANI/BN.

in adsorption capacity of all three metals was observed. As the initial solute concentration was fixed thus by increasing dosage quantity large surface area, greater availability of exchangeable sites was increased and adsorbate easily penetrates into adsorbent sites. When adsorbent mass was increased further from its optimum value, adsorption efficiency decreased due to overloading of adsorbent, resulting in overlying of binding sites and decrease in contact time required to attain equilibrium as adsorbent amount increases. The average values of adsorption of Cu, Pb, and Ni at different metal concentrations are 68%, 50%, and 75%. At different dosage amount, average values of adsorption of Cu, Pb, and Ni are 80%, 85%, and 70%.

Kinetic and thermodynamics studies

To investigate kinetic studies, pseudo-first order and pseudo-second order kinetics models were used. Kinetics of Cu, Ni, and Pb were studied at optimized conditions and by varying the contact time from 20 min to 60 min. Data were treated with pseudo-first and second order kinetics, but good results were obtained with pseudo-second order as mentioned in the literature (Robati 2013). Good correlation was found with pseudo-second order as shown in Figure 4(a). The following equation was used for pseudo-second order kinetics:

$$\frac{t}{qt} = \frac{1}{K_2 qe^2} + \frac{1}{qe} \cdot t$$

K_2 is pseudo-second order rate constant ($\text{gmol}^{-1} \text{min}^{-1}$), q_t is the amount of metal adsorbed (mgg^{-1}) at time (t); q_e is the amount of metal adsorbed at equilibrium (mgg^{-1}). An unsatisfactory correlation was found for pseudo-second order kinetics but the linear plot was found for pseudo-second order kinetics with correlation R^2 ranging from 0.93 to 0.99 for all the three metals under study, showing that the adsorption system follows pseudo-second order kinetics. The values of correlation coefficient R^2 for Pb, Cu, and Ni are 0.93, 0.94, and 0.99, respectively. The values of q_e for Pb, Cu, and Ni are 0.121, 0.03, and 0.06, respectively, and values of K_2 for Pb, Cu, and Ni are 200, 100, and 66.66.

The amount of adsorption of Cu, Ni, and Pb by PANI/BN composite was measured in a temperature range from 20 °C to 30 °C. Thermodynamic parameters, i.e., standard free energy ΔG° , standard enthalpy ΔH° , and standard entropy ΔS° were determined using the following equation (Moreno-Pirajan & Giraldo 2008; Anirudhan & Suchithra 2010):

$$\Delta G = RT \ln K_c, \quad \Delta H = \Delta G + T \Delta S, \quad \Delta S = \Delta G - (\Delta H/T)$$

Values of $T \Delta S$ intercept and ΔH were obtained from the above equation and slope of graph. The PANI/BN composite showed better adsorption of heavy metals than sawdust walnut adsorbent for thermodynamic parameters like entropy and enthalpy (Yasemin & Zeki 2007). Thermodynamic values for all the three metals are shown in Table 2. The negative values of ΔH° depict that reaction is

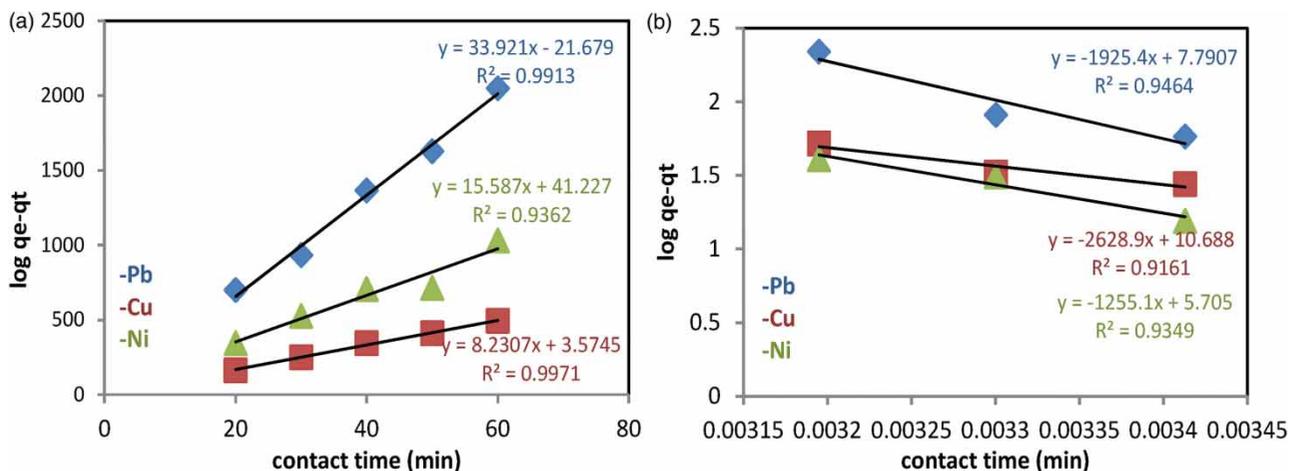


Figure 4 | Kinetic study of pseudo-second order kinetics (a) and effect of thermodynamic studies (b) on correlation coefficient (R^2) values of Pb, Cu, and Ni.

Table 2 | Effect of temperature on thermodynamic studies of Ni, Cu, and Pb metals

Temp K	Thermodynamics of Ni			Thermodynamics of Cu			Thermodynamics of Pb		
	dG	dH	dS	dG	dH	dS	dG	dH	dS
293	-4.297	6.39	4.68	-3.51	2.19	0.771	-2.90	4.89	3.67
303	-4.815	5.87	3.86	-3.83	1.87	0.310	-3.76	4.02	2.59
313	-6.09	4.59	4.59	-4.46	1.23	0.45	-4.19	3.60	1.96

exothermic for all three metals. Figure 4(b) shows the values of correlation coefficient R^2 for Pb, Ni, and Cu as 0.8945, 0.7824, and 0.8122, respectively.

Negative values of ΔG show spontaneity and feasibility of reaction at higher temperature. Positive value of entropy shows that the system's randomness increased after the adsorption of metals. Negative values of Gibbs free energy suggest the spontaneity and the feasibility of the adsorption. As shown in Table 2, the values of Gibbs free energy decrease with increase in temperature thus decreasing the spontaneity of the system.

Adsorption isotherms

Adsorption of metals on PANI/BN was also investigated through isotherm studies. Metal ions' distribution in solution phase and solid phase is explained by using the Langmuir isotherm, Freundlich isotherm, and Temkin isotherm as described for some other materials in the literature (Yang et al. 2013).

Freundlich, Temkin, and Langmuir isotherms

These isotherms can explain adsorption of different compounds, either organic or inorganic, on a wide range of adsorbents. The Freundlich adsorption isotherm in Figure 5(a) shows a relation between solute concentration in liquid phase (in which solute is in contact with) to the solute concentration in liquid phase. As shown in Table 3, the constant of the Freundlich isotherm (K_f) for Cu, Ni, and Pb is 1.0453, 0.01588, and 0.0172, respectively. The values of correlation coefficient (R^2) for heavy metals Cu (0.8818), Ni (0.9082), and Pb (0.9212) are near to linearity.

The graph of $\log q_e$ versus $\log C_e$ for the Freundlich adsorption isotherm for all metals shows a linear line. The highest regression value was found for Pb with a value of

0.92, and 0.90 and 0.88 for Ni and Cu, respectively. The values of n were also greater than unity which further increases the reliability of adsorption.

As shown in Figure 5(b), the Temkin isotherm value for different metals is near to unity, the adsorption capacity of PANI/BN-based adsorbent is much higher than that of the unfunctionalized PANI/BN at corresponding conditions. The Temkin equation shows a good fit for the adsorption isotherms, which implies a monolayer adsorption of Cu(II), Ni, and Pb onto the homogeneous surface of the adsorbents. The PANI/BN-based adsorbent has an excellent absorption capacity for different metals as shown in the Temkin isotherm; the maximum adsorption for lead was found with R^2 value 0.98 and for Ni and Cu it was 0.97 and 0.96, respectively. The graphs of all the metals studied show good linear graphs for the Temkin isotherm and values of regression coefficient can be observed from Table 3.

Figure 5(c) shows a linear plot of $\frac{C_e}{q_e}$ versus C_e (constant of equilibrium in solution) for various initial concentrations of Cu, Ni, and Pb, proving that the data confirm to the Langmuir isotherm. In the case of Ni there are some deviations from linearity which is due to the nature of that metal. The values of correlation coefficient (R^2) for Cu (0.92), Ni (0.94), and Pb (0.78) suggested that they have a better adsorption process than other metals like Zn and Mn using this material. Table 3 demonstrates the R_L values and proves that spontaneous endothermic adsorption is the key characteristic of PANI/BN-based adsorbent for heavy metals.

CONCLUSIONS

PANI/BN-based adsorbent was synthesized by bonding polyaniline and bentonite for water remediation and their structures were characterized by SEM and FTIR. The results

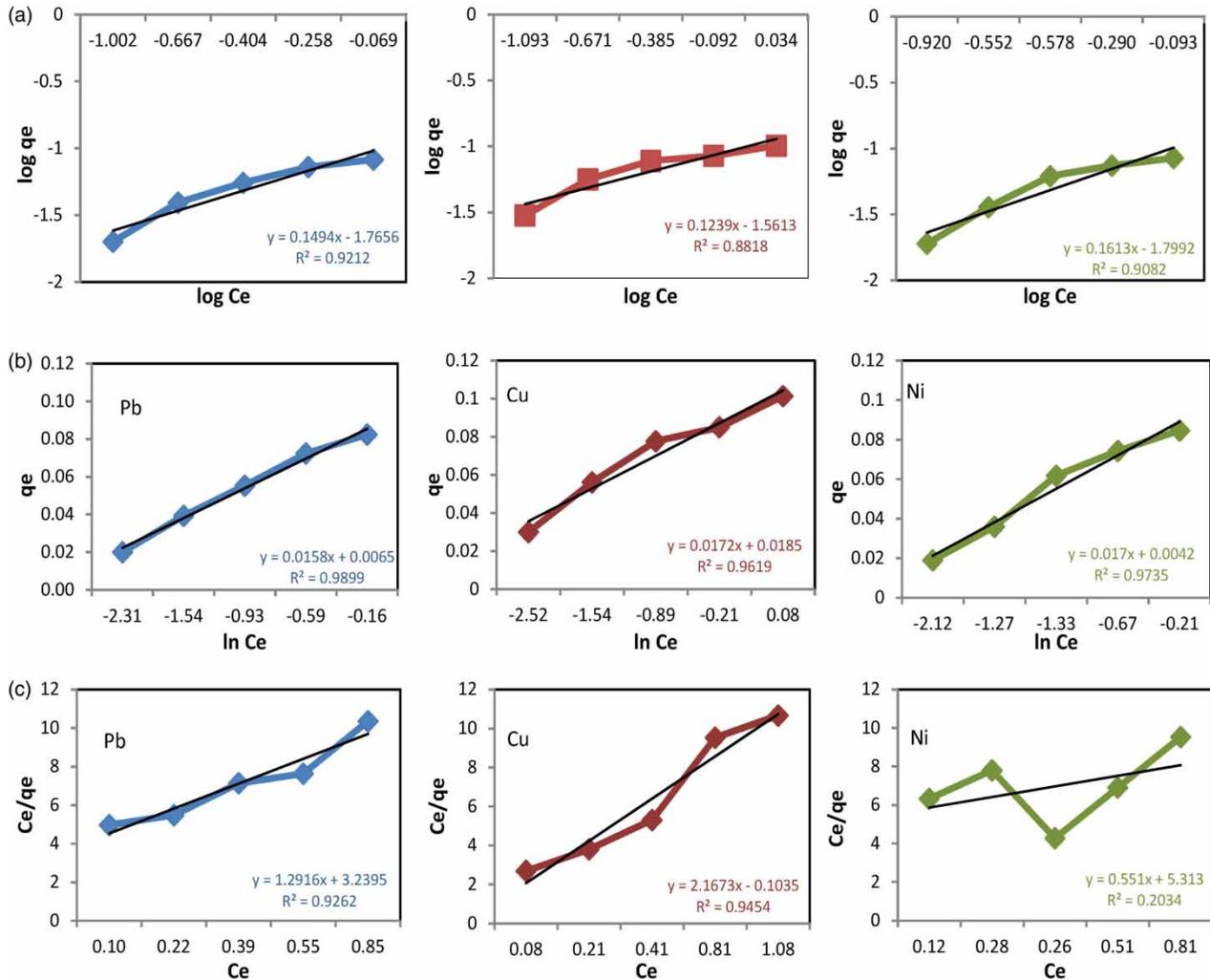


Figure 5 | Adsorption effect of Freundlich (a), Temkin (b), and Langmuir (c) isotherm curves for Pb, Cu, and Ni.

Table 3 | Adsorption effect of Freundlich, Temkin, and Langmuir isotherms for heavy metals

Metals	Freundlich isotherm			Temkin isotherm			Langmuir isotherm			
	K_f	N	R^2	A	B	R^2	Q_e	B	R^2	R_L
Cu	1.0453	1.4614	0.8818	1.117	1,143.16	0.9619	0.303	0.391	0.9262	0.99
Ni	0.01588	6.199	0.9082	1.766	145,741	0.9735	0.461	0.477	0.9454	0.99
Pb	0.0172	6.711	0.9212	2.57	156,772	0.9899	0.4712	0.488	0.787	0.99

indicated that PANI/BN-based absorbent has an excellent Cu, Pb, and Ni adsorption performance, and the highest binding capacity, as binding capacity of 130 mg g^{-1} for Ni was observed under normal conditions. The adsorption of PANI/BN absorbent was dependent on pH, a higher pH was

favorable for removal of Pb, Cu, and Ni, while ionic strength has no apparent effect. The adsorption isotherms and adsorption capacity for heavy metals at 20°C , 30°C , and 40°C temperature with optimum pH 5 for Pb, 6 for Cu, and 7 for Ni has proven that PANI/BN-based absorbents are an efficient

source of water treatment. The adsorption at optimum pH for Cu (pH 6), Pb (pH 5), and Ni (7) was observed as 85 mg g^{-1} , 105 mg g^{-1} , and 130 mg g^{-1} , respectively. Percentage removal efficiency of heavy metals Pb (98%), Cu (82%), and Ni (99%) has proved to be increased under optimized conditions. The Langmuir isotherm model and pseudo-second order equation has confirmed that adsorption took place, and adsorption capacity reached its maximum with pH 7 for Ni. The uptake of Pb, Cu, and Ni was enhanced by PANI/BN-based absorbent and polyaniline-bentonite composite acted as a potential adsorbent for efficient removal of Pb, Cu, and Ni. It is expected that the proposed PANI/BN-based absorbent can be used for the removal of hazardous substances in practice.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of this project by the National Science Foundation of China (21575113), the State Key Laboratory of Analytical Chemistry for Life Science (SKLACLS1811), and the Natural Science Fund of Shaanxi Province in China (2017JM2036).

REFERENCES

- Anirudhan, T. S. & Suchithra, P. S. 2010 Equilibrium, kinetics and thermodynamics modeling for the adsorption of heavy metals on chemically modified hydrotalcite. *Indian Journal of Chemical Technology* **17** (4), 247–259. [http://nopr.niscair.res.in/bitstream/123456789/9995/1/IJCT%2017\(4\)%20247-259.pdf](http://nopr.niscair.res.in/bitstream/123456789/9995/1/IJCT%2017(4)%20247-259.pdf).
- Duncan, A. E., Vries, N. D. & Nyarko, K. B. 2018 Assessment of heavy metal pollution in the sediments of the River Pra and its tributaries. *Water Air and Soil Pollution* **229**, 272. <https://doi.org/10.1007/s11270-018-3899-6>.
- Gupta, V. K. & Ali, I. 2004 Removal of lead and chromium from wastewater using bagasse fly ash – a sugar industry waste. *Journal of Colloid Interface Science* **271**, 321–328. <http://doi.org/10.1016/j.jcis.2003.11.007>.
- Hostermen, J. W. & Patterson, S. H. 1992 *Bentonite and Fuller's Earth Resources of United States*. Report U.S. Geological Survey, Washington, DC, USA. <https://pubs.usgs.gov/pp/1522/report.pdf>.
- Khan, K., Lu, Y., Khan, H., Zakir, S., Ihsanullah Khan, S., Khan, A. A., Wei, L. & Wang, T. 2013 Health risks associated with heavy metals in the drinking water of Swat, northern Pakistan. *Journal of Environmental Science* **25** (10), 2003–2013. [https://doi.org/10.1016/S1001-0742\(12\)60275-7](https://doi.org/10.1016/S1001-0742(12)60275-7).
- Mehwish, A., Sajjad, H. & Abdul, J. B. 2013 Adsorption of lead and copper from aqueous solution using unmodified wheat straw. *Environmental Engineering and Management Journal* **12** (11), 2117–2124. <https://www.researchgate.net/publication/262162359>.
- Meneghel, A. P., Gonçalves, J. A. C., Tarley, C. R., Stangarlin, J. R., Rubio, F. & Nacke, H. 2014 Studies of Pb²⁺ adsorption by *Moringa oleifera* Lam. seeds from an aqueous medium in a batch system. *Water Science and Technology* **69** (1), 163–169. <https://doi.org/10.2166/wst.2013.627>.
- Moreno-Pirajan, J. C. & Giraldo, L. 2008 Isothermic titration calorimetry as a tool for the prediction of thermodynamic property of cyclodextrin. *Energies* **1**, 93–104. <https://doi.org/10.3390/en1030093>.
- Robati, D. 2013 Pseudo-second-order kinetic equations for modeling adsorption systems for removal of lead ions using multiwalled carbon nanotube. *Journal of Nanostructure in Chemistry* **3** (55), 1–6. <https://link.springer.com/content/pdf/10.1186%2F2193-8865-3-55.pdf>.
- Wang, Y. G., Huang, S. J., Kang, S. F., Zhang, C. L. & Li, X. 2012 Low-cost route for synthesis of mesoporous silica materials with high silanol groups and their application for Cu(II) removal. *Materials Chemistry and Physics* **132** (2–3), 1053–1059. <https://doi.org/10.1016/j.matchemphys.2011.12.064>.
- Xiong, C., Yao, C., Wang, L. & Ke, J. 2009 Adsorption behavior of Cd (II) from aqueous solutions onto gel-type weak acid resin. *Hydrometallurgy* **98** (3–4), 318–324. <https://doi.org/10.1016/j.hydromet.2009.05.008>.
- Yang, W., Ding, P., Zhou, L., Yu, J., Chen, X. & Jiao, F. 2013 Preparation of diamine modified mesoporous silica on multi-walled carbon nanotubes for the adsorption of heavy metals in aqueous solution. *Applied Surface Science* **282**, 38–45. <https://doi.org/10.1016/j.apsusc.2013.05.028>.
- Yang, S., Sun, X., Shen, Y., Chang, C., Guo, E., La, G., Zhao, Y. & Li, X. 2017 Tolerance and removal mechanisms of heavy metals by fungus *pleurotus ostreatus* HAAS. *Water Air and Soil Pollution* **228**, 130. <http://doi.org/10.1007/s11270-016-3170-y>.
- Yasemin, B. & Zeki, T. 2007 Removal of heavy metals from aqueous solution by sawdust adsorption. *Journal of Environmental Sciences* **19** (2), 160–166. [https://doi.org/10.1016/S1001-0742\(07\)60026-6](https://doi.org/10.1016/S1001-0742(07)60026-6).
- Yavuz, A. G., Dincturk-Atalay, E., Uygun, A., Gode, F. & Aslan, E. 2011 A comparison study of adsorption of Cr (VI) from aqueous solutions onto alkyl-substituted polyaniline/chitosan composites. *Desalination* **279** (1–3), 325–331. <https://doi.org/10.1016/j.desal.2011.06.034>.
- Zhai, Y., Xu, X., Wang, H., Shi, X. & Lei, D. 2015 Adsorption of copper on tri-amino-functionalized mesoporous delta manganese dioxide from aqueous solution. *Water Science and Technology* **71** (5), 747–753. <http://doi.org/10.2166/wst.2015.020>.