Adsorption isotherms and kinetics pertinent to modified composite hydrogel adsorbents adopted for heavy metals removal

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ABSTRACT

Environmental friendly adsorbents constitute an effective method for heavy metals pollution mitigation. In this work, batch adsorption experiments were conducted for the adsorption of various heavy metals including Cr, Co, Ni and Pb using cost-effective modified adsorbents. These comprise polyacrylate hydrogels prepared using microwave (M) irradiation technique (ACM) or ultrasonic (U) irradiation technique (ACU). Further blends of acrylic acid salts with Egyptian kaolin (AKM and AKU) or zeolite (AZM and AZU) were also investigated. The effect of pH and initial concentration on the performance of the composite hydrogels has been studied. Also, several adsorption isotherm and kinetic models were studied. AKU revealed the highest maximum adsorption capacities among other investigated composites for all the tested heavy metals. The equilibrium adsorption experiments revealed that Langmuir isotherm model is best fitted than other models with maximum adsorption capacities of 84.5, 73.3, 61 and 97 mg/g for Cr, Co, Ni and Pb, respectively and equivalent results were obtained from Tempkin isotherm for all ions except Ni. Adsorption kinetics of Cr, Co, Ni and Pb using all the composite hydrogels were best described with the Pseudo-second order kinetic model.

Keywords: Heavy metals, Cost-effective, Composites, Adsorption isotherm, Kinetics.

1. INTRODUCTION

Heavy metals pollution is receiving increasing endeavors from the research community in recognition of its documented serious effects on health and the environment. Current practices for the removal of hazardous heavy metals comprise adsorption, precipitation, coagulation, ion exchange and membrane techniques (Barakat, 2011; Emamjomeh and Sivakumar, 2009; Esalah et al., 1999; Ghurye et al., 2004; Mahmoud and Hoadley, 2012; Yurlova et al., 2002). Adsorption technology is one of the cornerstones for alleviating heavy metal pollution episodes (Barakat, 2011; Renu and Singh, 2017). Further, some situations dictate the siting of the adsorption unit upstream or downstream of the treatment line. Numerous endeavors for improving the performance and stability of adsorbents comprise, but not limited to, enhancing the effectiveness of current commercial adsorbents, developing new promising organicinorganic hybrid polymers (Bhatia et al., 2017; Inagaki et al., 2007; Liu et al., 2012; Zhao et al., 2010). Ecofriendly green adsorbents based on modified natural polymers and their composites are now the focus of numerous research groups around the world. These green adsorbents comprise for example chitosan, cellulose ones, alginates (Gomez-Maldonado et al., 2019). Modified clays and zeolite adsorbents are also used in current practices (Renu and Singh, 2017). One of the materials that is gaining wide acceptance is hydrogel which has numerous advantages for heavy metals removal. These



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include hydrophilicity, dimensional stability, minimum toxicity, the multiplicity of functional groups that could be attached to the base polymer and biodegradability which facilitates final disposal of exhausted adsorbates (Elsayed, 2019; Sezgin and Balkaya, 2016). The performance of clay/hydrogel composites for hardness and heavy metals removal from their solutions have been studied by several authors (Bulut et al., 2009; Liu et al., 2015; Natkański et al., 2012; Sorour et al., 2018; Sorour et al., 2020). For instance, lead removal by polyacrylic acid-organo-bentonite nanocomposite, polyacrylic acid hydrogel beads and sodium polyacrylate-bentonite material approached 93 mg/g (Rafiei et al., 2016), 113 mg/g (Al-Abachi, 2013), and 70 mg/g (He et al., 2016a). Moreover, Cu, Zn, Cd and Mn were successfully removed by sodium polyacrylatehumic acid rectorite composite (Chen et al., 2012) and kaolinite containing polyacrylic acid-co-acrylamide hydrogels (Atia et al., 2009). Besides, polysaccharidezeolite, zeolite acrylamide maleic-acid and chitosan-zeolite Na-X based composites have been studied for the removal of Cu, Cd, Pb and Zn (Akkaya and Ulusoy, 2011; Djelad et al., 2016; Zhang and Wang, 2015).

With such increasing interest and practice of green adsorbents, it deemed necessary to investigate the applicable isotherm and pertinent kinetic models to a newly developed cost-effective composite hydrogel incorporating tailored blending of kaolin or zeolite to microwave/ultrasonic processed polyacrylate hydrogels.

This work investigates the adsorption performance of the previously prepared polyacrylate coated kaolin/zeolite composite hydrogels for the removal of Cr, Co, Ni and Pb from their synthetic solutions. In addition, the adsorption isotherm models and kinetic study were thoroughly investigated and compared.

2. MATERIALS AND METHODS

2.1 Materials

In house prepared hydrogel composite samples reported by the authors (Sorour et al., 2018; Sorour et al., 2020), were used as cost-effective adsorbents in this study. These comprise polyacrylate hydrogels prepared using microwave (M) irradiation technique (ACM) or ultrasonic (U) irradiation technique (ACU). Further, blends of acrylic acid and Egyptian kaolin (AKM and AKU) or zeolite (AZM and AZU) were also investigated. Investigated heavy metal ions include Cr, Co, Ni and Pb and their salts were used for the preparation of synthetic solutions. CoCl₂ (Shantou Guanghua Chemical Factory Co., Ltd), Cr(NO₃)₃.6H₂O (PRS Panareac Quimica Sa), NiCl₂.6H₂O (S.d.fine-chem Ltd.) and Pb(CH₃COO)₂·3H₂O were used. Hydrochloric acid and sodium carbonate were used for pH adjustment.

2.2 Adsorption Studies

Adsorption experiments were conducted using the batchmode technique with pH variation (4-8.5) (Dean et al., 1972) as measured by a pH meter (HANNA apparatus model-211). All the samples mentioned in section 2.1 were investigated and their particle size was below 850 μ m. They were added to the prepared heavy metal ions containing single system solutions in appropriate flasks. The flasks were sealed and constantly shaken using a water bath shaker (Julabo, SW-20C) with constant stirring (150 rpm) at 27°C. Adsorption was performed for Cr Co, Ni and Pb in their synthetic solutions at initial concentration (C_i) 10-100 mg/L. Adsorption time ranged from 10 min up to 24 h. The supernatant was separated by filtration technique using a Whatman filter paper no. 4 and analyzed to determine the concentration of the residual elements in solution.

Concentrations of ions before and after treatment were measured using an atomic absorption flame spectrometer (GBC, Avanta). The adsorption capacity (q) was calculated using the following equation (Green, 2008; Hani, 2010):

$$q = \frac{c_i - c_e}{m} \times V \tag{1}$$

Where, q is the amount of metal ions adsorbed in (mg/g of dry adsorbent), C_i and C_e are the initial and equilibrium ion concentrations (mg/L), respectively; V is the volume of metal ions solution used (L), and m is the weight of dry adsorbent (g).

2.3 Adsorption Isotherm Models

Several equilibrium models were investigated including Langmuir, Freundlich, Dubinin-Radushkevich, Tempkin and Florry-Huggins isotherms (Ayawei et al., 2017; Foo and Hameed, 2010; Nechifor et al., 2015; Shikuku et al., 2018). Langmuir isotherm assumes monolayer adsorption using a surface with a finite number of identical sites, Freundlich isotherm; interprets the adsorption on heterogeneous surfaces with interactions occurring between the adsorbed molecules and is not restricted to the formation of a monolayer. Moreover, Dubinin-Radushkevich (D-R) isotherm assumes that the adsorption has a multilayer character and involves Vander Waals forces. While Tempkin and Florry-Huggins isotherms evaluate the adsorption potential of the adsorbent and adsorbate. Table 1 summarizes each of the pre-mentioned models with their parameters.

For the quick prediction of isotherm profile, a tailored software has been developed, tested and evaluated using Visual Basic (version 10) software and used for fitting and parameters estimation of all isotherm models.

2.4 Kinetic Study of the Adsorption Process

The kinetic models of sorption that define the adsorption rate, mechanism and optimum sorption time are investigated. These include Pseudo first and second order and Elovich kinetic models (Qiu et al., 2009; Wang and Guo, 2020; Yakout and Elsherif, 2010). The Pseudo-first-order model is the most widely used rate equation in liquid phase sorption. It assumes that the rate of change of sorbate uptake with time is directly proportional to the difference in the saturation concentration and the amount of solid uptake

Table 1. Summary of investigated adsorption isotherm and kinetic models								
Model	Nonlinear form	Linear form	Plot	Constants	Ref.			
	q _e	$\frac{1}{q_e} = \frac{1}{b * q_m} + \frac{C_e}{q_m}$	$\frac{1}{q_e}$ vs. $\frac{1}{C_e}$	b, q _m	Ayawei et al.			
Langmuir	$= q_{m} \\ * \frac{b * C_{e}}{1 + b * C_{e}}$	$\frac{C_{e}}{q_{e}} = \frac{1}{q_{m}} + \frac{1}{C_{e} * b * q_{m}}$	$\frac{C_e}{q_e}$ vs. C_e	b, q_m	(2017), 100 and Hameed (2010); Shikuku et al. (2018)			
Freundlich	$q_e = K_F * C_e^{1/n}$	$\log q_e$ $= \log K_F + \frac{1}{n} \log C_e$	log q _e vs. log C _e	K _F , n	Ayawei et al. (2017); Foo and Hameed (2010); Shikuku et al. (2018)			
Dubinin- Radushkevich (D-R)	$q_e = q_s \\ * \exp(K_{ad} * \zeta^2)$	$ln(q_e) = ln(q_s) - (K_{ad} + \zeta^2)$	$\ln(q_e)$ vs. ζ^2	K_{ad}, E $= RT$ $* \ln(1 + \frac{1}{C_e})$ $E = \frac{1}{\sqrt{2 + K}}$	Ayawei et al., (2017); Foo and Hameed (2010)			
Tempkin	$q_{e} = \frac{R * T}{b_{T}} * \ln(A_{T} * C_{e})$	$q_e = \frac{R * T}{b_T} \ln(A_T) + \frac{R * T}{b_T} \ln(C_e)$	q _e vs.ln(C _e)	$b_{\rm T}, A_{\rm T}$	Ayawei et al. (2017); Foo and Hameed (2010); Nechifor et al. (2015); Shikuku et al. (2018)			
Florry-Huggins	$ \begin{aligned} & \frac{\theta}{C_i} \\ &= K_{FH} \\ &* (1 - \theta)^{n_{FH}} \end{aligned} $	$log \frac{\theta}{C_i} = log K_{FH} + n_{FH} log(1 - \theta)$	$\log \frac{\theta}{C_i} \text{vs.} \log(1 - \theta)$	$K_{FH}, n_{FH}, \Delta G$ ΔG $= -RT$ $* \ln(K_{FH})$	Ayawei et al. (2017); Foo and Hameed (2010); Nechifor et al. (2015)			
Table 2. Summary of investigated adsorption kinetic models								
Model	Nonlinear for	m Linear form	Plot	Constants	Ref.			
Pseudo-first-order	$\frac{dq_{t}}{dt} = k_{1} * (q_{e})$ $- q_{t})$	$\log(q_e - q_t)$ $= \log(q_e) - \frac{k_1}{2.303}$	$\log(q_e-q_i)$ vs. * t t	k1	(Qiu et al., 2009; Wang and Guo, 2020; Yakout and Elsherif, 2010)			
Pseudo-second-order	$\frac{dq_t}{dt} = k_2 * (q_e - q_t)^2$	$\frac{t}{q_t} = \frac{1}{k_2} * \frac{1}{q_e^2} + \frac{1}{q_e} *$	t $\frac{t}{q_t}$ vs.t	k ₂	(Qiu et al., 2009; Wang and Guo, 2020; Yakout and Elsherif, 2010)			

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Table 2. Summary of investigated adsorption kinetic models							
Model	Nonlinear form	Linear form	Plot	Constants	Ref.		
Pseudo-first-order	$\frac{dq_t}{dt} = k_1 * (q_e) - q_t$	$log(q_e - q_t)$ = log(q_e) - $\frac{k_1}{2.303} * t$	$log(q_e-q_t)$ vs. t	\mathbf{k}_1	(Qiu et al., 2009; Wang and Guo, 2020; Yakout and Elsherif, 2010)		
Pseudo-second-order	$\frac{dq_t}{dt} = k_2 * (q_e - q_t)^2$	$\frac{t}{q_t} = \frac{1}{k_2} * \frac{1}{q_e^2} + \frac{1}{q_e} * t$	$\frac{t}{q_t}$ vs.t	k ₂	(Qiu et al., 2009; Wang and Guo, 2020; Yakout and Elsherif, 2010)		
Elovich	$\frac{\mathrm{d} q_{\mathrm{t}}}{\mathrm{d} \mathrm{t}} = \mathrm{a}_{\mathrm{e}} \ast \mathrm{e}^{\frac{-\mathrm{q} \mathrm{t}}{\mathrm{b} \mathrm{e}}}$	$\begin{aligned} & q_t \\ &= \frac{\ln a_e b_e}{b_e} + \frac{1}{b_e} \ln t \end{aligned}$	q _t vs.lnt	a _e , b _e	(Qiu et al., 2009; Wang and Guo, 2020; Yakout and Elsherif, 2010)		

with time. The Pseudo-second-order model describes a second-order rate of sorption, while Elovich's equation is also used successfully to describe second-order kinetics of the chemisorption process assuming that the actual solid surfaces are energetically heterogeneous. Table 2 summarizes investigated kinetic models in this study. Excel software was used for fitting and parameters estimation of kinetic models.

3. RESULTS AND DISCUSSION

3.1 Adsorption Performance of hydrogel composites Fig. 1 represents the adsorption capacities of different heavy metals at pH 4 and an initial concentration of 10 mg/L using the investigated adsorbents. It is deduced from Fig. 1 that the inclusion of kaolin and zeolite into the polyacrylate hydrogel structure enhanced Cr uptake especially for



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Fig. 1. Adsorption capacities of the composite hydrogels for different heavy metals (C_i 10 mg/L, pH 4)

microwave prepared hydrogel samples (by more than 80%) while; Co and Ni uptake was slightly increased after kaolin and zeolite addition. Moreover, Pb uptake increased for microwave and ultrasonic prepared samples using zeolite (27%) and kaolin (3%), respectively.

3.1.1 Effect of pH on adsorption

The pH dependence of adsorption from 4 to 8 is typically shown in Fig. 2. By increasing pH from 4 to 8 the adsorption differs which may be explained by the existence of the metal ions as different complexes in aqueous solutions at different pH values and the behavior of each will be different. Moreover, charges on the adsorbent itself vary according to pH and consequently, its adsorption behavior is different, which agrees with Wan Ngah et al. (2011). It is also clear from Fig. 2 that for the tested ions within the investigated pH range, AKU and AZM attained higher performance as compared to AKM and AZU, respectively. Moreover, AKU and AZM revealed comparable performance at this concentration at certain pH values where the performance of AKU is slightly higher for most of the ions as shown in Table 3. Accordingly, AKU and AZM were selected for subsequent adsorption studies at selected pH values.

3.1.2 Effect of Metal Concentration on Adsorption

The effect of metal ion concentration (10-100 mg/L) on adsorption is depicted in Fig. 3 using the most appropriate adsorbent and pH (depicted from the previous section), where average experimental values are represented (solid lines manifest adsorption capacities and dotted lines manifest removal efficiencies). The removal efficiency decreases with increasing initial metal concentration while the adsorption capacity increased. At low initial concentrations, the removal was higher due to the larger surface area and vacant sites of the composite adsorbent. At higher initial concentration, the ratio of the initial number of ions to the available sites was higher and as a result, the removal decreased which agrees with Hani (2010) and Liu et al., (2015). At the maximum studied metal concentrations (86-100 mg/L), AKU attained the highest loading rates (70, 71, 78 and 93 mg/g) and removal efficiencies (92, 78, 92 and 93%) for Cr, Co and Pb while maximum attained adsorption capacity for Ni was (78 mg/g) at an initial concentration of 85.7 mg/L. Regarding AZM, the maximum adsorption capacities for Cr, Co, Ni and Pb were 46, 46, 74 and 96 mg/g respectively, with corresponding removal efficiencies of 78, 79, 86 and 96% at metal concentrations range 58.5-100 mg/L.

Table 3. Highest performance of selected kaolin/zeolite composite polyacrylate hydrogels at different pH values (C = 10 mg/L)

		($C_i = 10 \text{ mg/I}$	_)				
	Cr		Со		Ni		Pb	
Composite hydrogel	Uptake (mg/g)	pН	Uptake (mg/g)	pН	Uptake (mg/g)	pН	Uptake (mg/g)	pН
AKU	9.1	5.4	9.77	7	9.68	6	9.93	4
AZM	8.6	5	9.83	6	9.64	6	10	5



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Fig. 2. pH dependence of heavy metals adsorption (Ci 10 mg/L)

3.2 Adsorption Isotherm Studies

Adsorption data of Cr, Co, Ni and Pb using AKU and AZM were analyzed using Langmuir, Freundlich, Dubinin-Radushkevich, Tempkin and Florry (as mentioned in section

2.3). Thus, adsorption isotherm plots and fittings as obtained from the developed software using Visual Basic are shown in Fig. 4. The coefficients for the linearized forms of the isotherms and correlation coefficients at optimum pH and concentrations are presented in Table 4.



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Fig. 3. Effect of heavy metal concentration on adsorption capacities and % removal at specified pH values. Solid lines: adsorption capacities, dotted lines: removal efficiencies

Analysis of the correlation coefficients in Table 4 shows that Langmuir isotherm is adequate to describe the adsorption data of Cr, Co, Ni and Pb for AKU and AZM. It is worth mentioning that Tempkin isotherm competes with Langmuir for Cr, Co and Pb using AKU composite. For Pb ions sorption using AZM, the Langmuir model shows comparable fittings (correlation coefficient 0.974) with Dubinin-Radushkevich (D-R) (0.947) and Tempkin isotherm (0.98), which is considered the highest. Calculation of adsorption energy (E) using the D-R isotherm model could be calculated only for Pb on AZM as it fits with the D-R isotherm. Thus, the calculated value of E for Pb is 10.9 kJ/ mol which lies in the typical range of bonding energy for ion-exchange mechanisms is 8–16 kJ/mol (El-Kamash et al., 2005; Hani, 2010). Thus, given the comparable values for the investigated isotherms, the Langmuir model (mostly the second form, as mentioned in Table 4) could be used safely for data analysis.

As shown in Table 4, q_m which is indicative of maximum adsorption capacities as depicted from Langmuir isotherm, are 97.2, 84.5, 73.3 and 60.9 mg/g, in the order of selectivity Pb > Cr > Co > Ni, respectively using the composite AKU. It is also worth mentioning that AZM revealed higher maximum adsorption capacity only for Pb as depicted from Langmuir isotherm (128 mg/g) as shown in Table 4.



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AKU











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Fig. 4. Adsorption isotherm plots and isotherms fittings via developed software

Several endeavors for analysis of adsorption data of Cu, Mn, Zn, Cd and Pb fitted with Langmuir isotherm using different polyacrylate based composites. Examples include the removal of Pb, Cd, Cu and Zn by sodium polyacrylatehumic acid rectorite composite (Chen et al., 2012), Cu, Mn, Zn by kaolinite containing polyacrylic acid-co-acrylamide hydrogels (Atia et al., 2009), Cu by sodium polyacrylate (Yu et al., 2015), Pb by polyacrylic acid bentonite composite (Rafiei et al., 2016), Pb and Cd on acrylate/ acrylamide copolymer/GO hydrogel (He et al., 2016b). On the other hand, removal of Pb by sodium polyacrylate bentonite was investigated by He et al. and concluded that the results could be fitted best with Freundlich isotherm (He et al., 2016a).

Tabl	e 4. isomeri					tion using composite in		yulogels	
Isotherm model	(r	(Co	N	Ni		Рб	
isotherm model	AKU	AZM	AKU	AZM	AKU	AZM	AKU	AZM	
Langmuir 1									
\mathbb{R}^2	0.921	0.973	0.941	0.897	0.801	0.173	0.88	0.974	
$q_m (mg/g)$	169	60	85.55	53.86	106.6	39.38	121.06	198.96	
b (L/g)	0.074	0.121	0.492	0.868	0.33	3.291	1.017	0.361	
Langmuir 2									
R ²	0.967	0.97	0.972	0.992	0.996	0.994	0.946	0.96	
$q_m (mg/g)$	84.5	37.28	73.3	38.81	60.87	57.26	97.22	128.7	
b (L/g)	0.205	1.78	0.49	-1.44	2.44	11.62	1.03	0.64	
Freundlich									
R ²	0.832	0.676	0.829	0.579	0.632	0.52	0.842	0.934	
$K_F (L/g)$	15.14	10.96	24.43	21.5	25.58	27.91	40.58	43.23	
n	1.821	2.54	2.63	4.71	3.04	3.95	2.38	1.562	
<u>D-R</u>									
\mathbb{R}^2	0.857	0.735	0.849	0.625	0.686	0.529	0.852	0.947	
q _s (mmol/g)	9.27	3.07	4.09	1.47	3.71	2.32	2.625	10.323	
E (kJ/mol)	10.18	11.4	12.71	16.42	13.174	15.46	13.45	10.912	
Tempkin									
R ²	0.965	0.62	0.929	0.615	0.662	0.628	0.919	0.98	
b _T (kJ/mol)	0.144	0.3	0.206	0.5	0.231	0.292	0.154	0.101	
$A_T (L/g)$	2.69	4.76	12.39	211.41	23.81	67.65	25.62	9.53	
Florry Huggins									
R ²	0.49	0.84	0.695	0.788	0.639	0.501	0.602	0.598	
K _{FH} (L/mg)	6	4.9	6.7	8.1	5.6	9.53	4.23	0.268	
$\Delta G (kJ/mol)$	12.67	13.18	12.39	11.92	12.84	11.53	13.54	20.38	

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Table 4. Isotherm	parameters for	or heavy	metals adsor	ption us	sing com	posite h	vdrogel
				percir en		p 0 0 1 0 0 11	,

3.3 Adsorption Kinetic Studies

Adsorption kinetics were studied for the selected adsorbent from 10 min to 24 h. Results are presented in Fig. 5. Generally, the amount of metals adsorbed increases rapidly in the first hour and continues to increase up to 3 h for Pb, and 5 h for Cr, Co and Ni, beyond which, there is a minimum increase (2-5%) of the adsorption capacity. This trend could be explained by the initial rapid uptake of metal ions and subsequent slow kinetics into the remaining vacant sites where repulsive forces of the initial adsorbed layer tend to minimize the removal of metal ions on the remaining free sites (Green, 2008; Wang and Guo, 2020). Therefore, 3 h is chosen as the optimum contact time for Pb and 5 h for the other ions.

Also, the kinetic data were fitted using Excel software (for linear curve fitting) with Pseudo-first-order, Pseudo second-order and Elovich kinetic models. The values of the calculated kinetic data for AKU are listed in Table 5.

Moreover, AZM values were very close to AKU regarding Ni and Pb. The Pseudo second-order model is considered more appropriate for depicting the adsorption processes of AKU and AZM. It is worth mention that the Elovich model competes with the Pseudo second-order model only for Cr. AKU adsorbent could be thus considered the optimum composite adsorbent.

Several accomplishments for analysis of adsorption data of different ions fitted with Pseudo second-order kinetics model using different polyacrylate based composites. For example, the removal of Pb and Cd by sodium polyacrylatehumic acid rectorite composite (Chen et al., 2012), Cu by sodium polyacrylate (Yu et al., 2015), Mn, Cu, Zn on kaolinite containing polyacrylic acid-co-acrylamide hydrogel (Atia et al., 2009) and Pb on sodium polyacrylate bentonite (He et al., 2016a). On the other hand, removal of Pb and on acrylate/ acrylamide copolymer/GO hydrogel fitted with first-order kinetics model (He et al., 2016b).



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Fig. 5. Effect of contact time on heavy metals adsorption using selected composite hydrogels

1401	e 5. Kinetie pa	indificters it	n neuvy metals au	solption usi	ing optimum <i>i</i>	ixe composite ny	yurogens	
	Pseudo fir	st order	Pseudo secon	d order		Elovich		
Ion	k ₁	D ²	\mathbf{k}_2	D ²	b _e	a _e	D ²	
	(1/min)	K	(g/mg.min)	K	(g/mg)	(mg/g.min)	K	
Cr	0.009	0.965	0.0006	0.998	0.0976	22.08	0.996	
Co	0.009	0.965	0.001	0.999	0.1388	377.65	0.910	
Ni	0.01	0.952	0.0003	0.998	0.0772	11.25	0.964	
Pb	0.0042	0.81	0.001926	0.999	0.313		0.891	

Table 5. Kinetic parameters for heavy metals adsorption using optimum AKU composite hydrogels

4. CONCLUSION

This work presented the results of a detailed study of the adsorption process for removal of Cr, Co, Ni and Pb ions from aqueous solution using developed hydrogel composite adsorbents comprising acrylic acid salts and its blends with Egyptian kaolin or zeolites. Optimum set of adsorption conditions have been developed for the investigated adsorbents including pH, ions concentration and adsorption time. Among the investigated isotherm models, Langmuir isotherm was found appropriate for describing adsorption results on real ground for the studied metal ions. Maximum adsorption capacity using the composite AKU were 97.2, 84.5, 73.3 and 60.9 mg/g and % removal 93, 92, 78 and 90% in the order of selectivity Pb > Cr > Co > Ni, respectively. For process design applications, contact time ranging from 3h to 5h should be adequate for acceptable separation efficiency. As regards to kinetic analysis, second order Pseudo kinetic model proved to be most appropriate for describing time dependence of ions removal. In conclusion, AKU adsorbent could be considered the optimum composite adsorbent.

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NOMENCLATURE

Abbreviation	
ae	initial adsorption rate in Elovich kinetic model (mg/g min)
A _T	Tempkin isotherm equilibrium binding constant (L/g)
b	Langmuir constant related to the energy of adsorption (L/g)
be	desorption constant in Elovich kinetic model (g/mg)
b _T	Tempkin isotherm constant related to heat of adsorption (kJ/mol)
Ce	Equilibrium ion concentrations (mg/L)

C_i	Initial ion concentrations (mg/L)
E	Energy of adsorption (kJ/mol)
1 _e	the rate constant of first order kinetic
K]	model (1/min)
1-	the second-order sorption rate constant
K ₂	(g/(mg.min))
K_{ad}	D–R isotherm constant (mol^2/kJ^2)
V	Freundlich constant characterizing
\mathbf{K}_{F}	adsorption capacity (L/g)
$K_{\rm FH}$	Equilibrium constant in Florry model
m	Weight of dry adsorbent (g)
	Freundlich constant characterizing
n	adsorption intensity
n _{FH}	Ions number occupying adsorption sites
	Amount of metal ions adsorbed in (mg/g
q	of dry adsorbent)
	Equilibrium solid phase concentration
qe	(mg/g)
	Langmuir constant related to the
$q_{\rm m}$	adsorption capacity (mg/g)
	D-R isotherm theoretical saturation
$\mathbf{q}_{\mathbf{s}}$	capacity (mmol/g)
	amount of metal ions adsorbed using the
q_t	adsorbents (mg/g) at time t
R	The gas constant (8.314 \times 10 ⁻³ kJ/K mol)
Т	Absolute temperature (K)
V	Volume of metal ions solution used (L)
θ	Degree of surface coverage and is = $(1 - 1)^{-1}$
	C_{e}/C_{i}
3	D–R isotherm constant
ΔĞ	Gibbs free energy (kJ/mol)

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