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KEYWORDS : montmorillonite, copper(II), adsorption, removal, acid activated, polymer/clay nanocomposite, XRD, TGA and IR analyses, Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich isotherms.

Removal of Copper from Aqueous Solutions by Adsorption on to The Montmorillonite Clay Mineral

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ABSTRACT

The study was carried out to examine the efficiency of natural raw clay (RC), its acid activated form (AAC) and functionalized polymer/clay nanocomposite (PCN) for the removal of Cu(II) from aqueous solutions. XRD, TGA and IR analyses were used to characterize the mineralogical compositions of the three adsorbents. Batch adsorption method was applied for optimumization of adsorption conditions viz., adsorbent dosage, contact time, effect of temperature, effect of pH and initial copper concentration. Residual $^{Cu2+}$ ions were determined using ICP-MS. Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich isotherm equations have been applied to analyze the obtained experimental data. The isotherms affinity order were determined. The maximum adsorption capacities for RC, AAC and PCN were found to be 7.22, 7.04 and 19.45 mg/g, respectively.

Introduction

Copper containing wastewaters are extensively released from different industries and its excessive entry into food chains results in serious health impairments, carcinogenicity and mutagenesis in various living systems [1]. Enhanced industrial activity during recent decades has led to the discharge of unprecedented volumes of wastewater, which is a serious cause of environmental degradation.

The excessive intake of copper by man leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, central nervous problems followed by depression, gastrointestinal irritation, and possible necrotic changes in the liver and kidney.

The cupric ion (Cu^{2+}) is the most toxic species[2]. (WHO) recommended a maximum acceptable concentration of Cu^{2+} in drinking water of 2 mg/L[3].

The prevalence of adsorption separation [4-16] in the environmental chemistry is owing to their low cost, effectiveness, sustainability, simplicity of design, ease of operation, insensitivity to toxic substances and complete removal of pollutants.

The high cost of activated carbon has motivated scientists towards the search for new low cost adsorbents. A large number of clays have been utilized as adsorbents: bio-inspired polydopamine coated natural zeolites [18], clinoptilolite [19], natural and conditioned clinoptilolites [20], Tunisian smectitic [21], bentonite [22] and clay minerals[23]. Several nanoparticles showed increased adsorption capacity and efficiency[24].

In the present work, the adsorption of Cu^{2+} ions onto natural raw clay, which is obtained from Gebel Qarara at Beni-Suef city, Egypt, was carried out. Acid activation by sulfuric acid and PCN were performed in order to improve the removal capacity.

EXPERIMENTAL

Raw clay was obtained from Gebel Qarara with Coordination Lat. 28º, 53'N and Long. 30º, 56'E), Beni-Suef, Egypt, and was grinded in a ball mill, sieved followed by milling the clay again to nano-sized clay. After that, it was purified by washing several times with deionized water, filtered and dried at 80°C over night.

Purified RC mineral was activated by refluxing with 1M H_2SO_4 at 80 °C for 2 hrs. The precipitate was washed with deionized water until the filtrate was free from SO_4^{2-} The precipitate was dried under vacuum at 90°C , grinded and stored.

Poly m-aminophenol/clay nanocomposites have been synthesized using a pseudo dispersion oxidative polymerization of m-aminophenol (mAP) in aqueous HCl medium using ammonium persulfate (APS) as oxidant. The dark brown precipitate of PCN obtained precipitate was filtered and washed 4–5 times with 4 M HCl , then with deionized water till neutral pH, finally dried at 60–70 °C in a vacuum oven.

Thermal Gravimetric Analysis (TGA) was conducted on a METTLER TOLEDO (model TGA/SDTA851e/LF/1100) from room temperature to 1000 °C with temperature rate 10 °C/min under N_2 flow with rate of 50 mL/min. X-ray diffraction (XRD) patterns were measured on an X'Pert Pro Multi Purpose X-Ray diffractometer (Philips PANalytical) equipped with a Cu K_α source operated at 40 kV, λ=1.5406 nm and 40 mA. The 2θ angle was scanned from 2 to 90 degree with a raising rate of 2º per min and a step size of 0.02º. FT-IR was performed using a PerkinElmer (Waltham, Massachusetts, U.S.A) spectrometer with a resolution of 8 cm^{-1} in the range of 4000 and 400 cm^{-1}. Inductively coupled plasma analysis mass spectroscopy (ICP-MS) was performed on ICP-MS Agilent A7700. The pH of the sorption solutions was adjusted by using pH meter (NEOMET: model DO-350L) from iSTEK Inc.

After each Batch experiment, aliquots of the treated samples were separated by filtration, followed by analysis of the filtrate for residual Cu^{2+} ions using ICP-MS.

Determination of the optimum adsorbent amount:

Initial metal concentrations of 85.74, 28.57 and 130 mg Cu^{2+}/L had pH 5.4 were used to optimize the adsorbent dosage for RC, AAC and PCN, respectively. Vigorous stirring was applied for one hour contact time at room temperature 25 °C. The concentration of the residual Cu^{2+} ions in the solutions was determined by ICP-MS.

Determination of the optimum agitation contact time: Contact time was investigated for 15, 30, 45, 60, 90, 120, 150 and 180 min. The reaction was done at room temperature 25 °C with optimized adsorbent dosage 0.4, 0.2 and 0.1 g for RC, AAC and PCN; respectively.

Determination of the effect of temperature: Temperatures 25, 30, 40, 50, 60 and 70 °C were investigated for each type of clay.

Determination of the optimum metal concentrations:

Initial metal concentrations 42.86, 57.14, 71.43, 85.71, 100, 114.29 and 128.57 mg Cu^{2+}/L for RC; 14.29, 28.57, 42.86, 57.14, 71.43, 85.71 and 100 mg Cu^{2+}/L for AAC and 15, 65, 80, 115, 130, 215 and 315 mg Cu^{2+}/L for PCN were performed at the optimum adsorbent dosage and agitation at pH 5.4 at room temperature 25 °C. The concentration of the residual Cu^{2+} ions in the solutions was determined by ICP-MS.

Determination of the optimum pH value:Initial pH values of solution were adjusted at 2, 3, 3.5, 4, 5, 6, and 7; and investigated

Volume : 3 | Issue : 7 | July 2014 • ISSN No 2277 - 8179

under the conditions of optimized contact time and adsorbent dosage.

Results and discussions

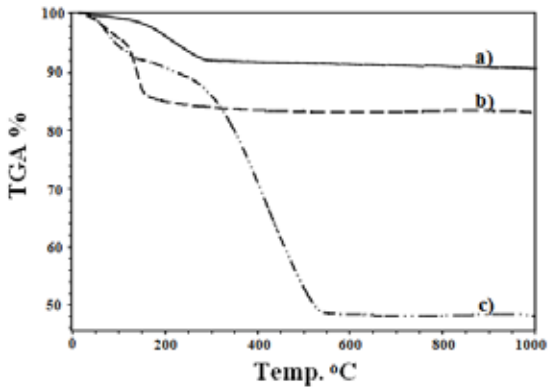

Figure 1. Thermal gravimetric analysis for a) RC, b) AAC and c) PCN.

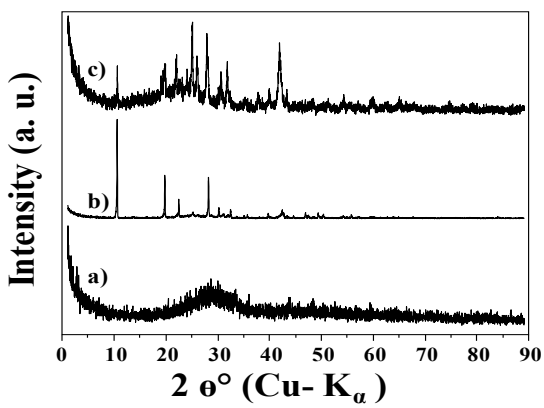

Figure 2. X-ray diffractograms of a) RC, b) AAC and c) PCN.

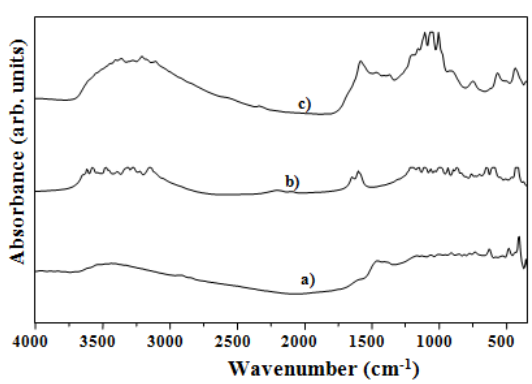

Figure 3. FT-IR spectra of a) RC, b) AAC and c) PCN.

In figure (1) TGA for RC and AAC reveal three weight loss steps. The first at the range 30 to 150 °C corresponds to the liberation of the mechanically held water. The second stage, 150 and 300 °C characterizes the dehydration of iron bearing minerals. The last one at 300 to 1000 ºC which confirms the evolution of the lattice hydroxyl groups of the clays as well as the dissociation of dolomite, with a weight loss of about 1.5 %. Four weight losses were recorded for PCN. The first, from 30 to 150 °C, corresponds to the mechanically held water. The second weight loss at 150 to 300 °C is attributed to the dehydration of iron bearing minerals and some decomposition products, which might be O_2 and H_2O molecules [24]. The third weight loss in the range 300 to 545 °C which is attributed to the total decomposition of poly (m-aminophenol) in the form of CO_2, NO_x and H_2O gases. The last weight loss of 1.8% from 545 to 1000 ºC which confirms the evolution of the lattice hydroxyl groups of the clays.

XRD patterns of the studied clay samples are shown figure (2). The results revealed that the investigated RC and PCN contain some quartz, montmorillonite, illite, kaolinite, and dolomite. For AAC, the kaolinite is converted to gypsum which is the main cause for decreasing the removal efficiency for AAC. On the other hand, montmorillonite and kaolinite represent the major clay minerals content of the studied samples.

The characteristic vibrational bands obtained from FTIR spectra of PCN figure (3) proved the successful preparation of the poly meta-aminophenol[25]. A broad band appears in the region 3690–1833 cm^{-1} which is due to the stretching of aromatic C–H, hydrogen bonded –OH, and –NH– groups. The –OH group is hydrogen bonded with nearest nitrogen of –NH group present in the polymer chain. So –OH absorption band appears at about 3425cm^{-1} as a broad peak. There is a band at 1050 cm^{-1} due to bending vibration of aromatic C–O–H group present in the polymer. The band at 1236 cm^{-1} is close to C–O stretching band at 1265cm^{-1} as an overlapping broad band. Due to the band at 1050 cm^{-1} and a very weak band at 1236 cm^{-1}, it is expected that very little C–O–C linkage was formed in the polymer. That means most of the –OH groups remain free after polymerization.

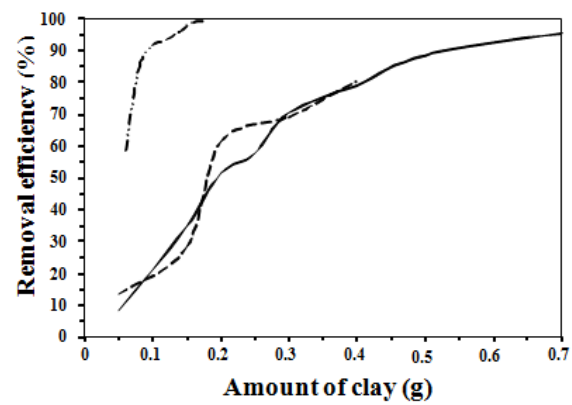

Figure 4. Effect of the adsorbent dosage on the adsorption of Cu^{2+} ions ;) RC, b) AAC and) PCN.

The effect of dose for each of the three adsorbents on the percentage removal of Cu^{2+} ions was shown in figure (4). The optimum dosage was 0.4, 0.2 and 0.1 g that achieved removal efficiency 79.06%, 61.26% and 91.34% for RC, AAC and PCN, respectively.

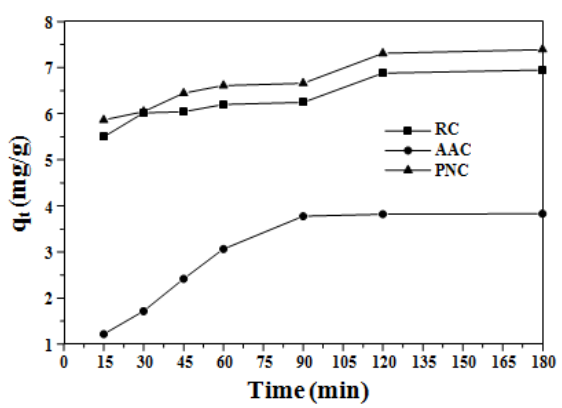

Figure 5. Effect of the contact time on the adsorption of Cu^{2+} ions on the different types of clay.

The higher amount of adsorption capacity by PCN around 7.31 mg/g could be rationalized in terms of increasing both the ac-

tive sites and the surface area according to the presence of the polymer chains.

The relationship between adsorption capacity and adsorption time represented in figure (5) is used to describe the adsorption kinetics. In order to analyze the adsorption mechanism of Cu^{2+} ions onto the different types of clay; Lagergren pseudo-first-order and pseudo-second-order [26-29] adsorption kinetics models were applied to fit the obtained experimental data and investigate the adsorption properties of each adsorbent.

The calculated kinetic parameters for adsorption of Cu^{2+} ions onto the different types of clay are listed in Table 1.

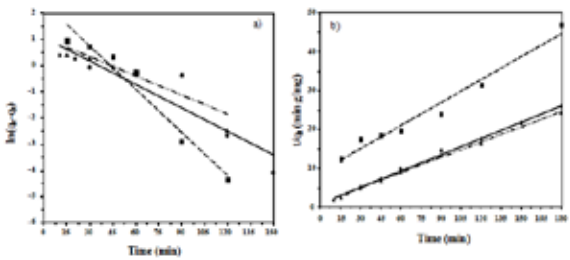

Figure 6. The first-order Lagergren kinetic model (a) and second-order kinetic model (b); for RC (♦——), for AAC (■– – –) and for PCN (▲–··–·–).

Table 1. Kinetic model parameters for the adsorption of Cu^{2+} ions onto RC, AAC and PCN:

Kinetic models	Parameters	RC	AAC	PCN
Pseudo first-order	K_1 (min)	0.02994	0.05475	0.02432
	q_e cal. (mg/g)	2.97722	10.72996	2.89021
	S.D.	0.65655	0.52226	0.53834
	R^2	0.85896	0.95457	0.79600
Pseudo second-order	K_2 (g/mg min)	0.02120	0.00435	0.01615
	q_e cal. (mg/g)	7.15154	5.04185	7.66107
	S.D.	0.45842	2.23261	0.41837
	R^2	0.99742	0.96928	0.99744
Experimental	q_e Exp. (mg/g)	6.8776	3.8155	7.3074

Referring to Table 1, the correlation coefficients (square of regression (R^2) values close or equal to 1) is an expression for the conformity between the experimental data and the model.

Isotherm Analysis:

For analyzing the experimental data, adsorption isotherm models were used to determine the homogeneous and heterogeneous characteristics. To evaluate the adsorption isotherm, four equilibrium isotherms were studied: (A) Langmuir, (B) Freundlich, (C) Tempkin and (D) Dubinin-Radushkevich. Analysis of isotherms was used to describe the experimental adsorption data, and then best results can be obtained when correlation coefficients (R^2) come close to 1, Table 3. High values of R^2 (close or equal to 1) indicate the conformity among experimental data with the isotherm model.

Table 2. Equilibrium isotherm model parameters for the adsorption of Cu^{2+} ions onto RC, AAC and PCN:

Equilibrium models	Parameters	RC	AAC	PCN
Langmuir	Q_m (mg/g)	7.2228	7.0398	19.452
	K_L (L/mg)	1.1362	0.1448	0.0635
	S.D.	0.1942	0.1142	0.6347
	R^2	0.9946	0.9989	0.9882
Freundlich	K_F (mg/g) $(L/mg)^{1/n}$	5.2815	1.6332	4.1229
	n_F	13.023	2.8279	3.5902
	S.D.	0.0569	0.1446	0.0438
	R^2	0.9527	0.8996	0.9973
Tempkin	A_T (L/mg)	28.756	1.8037	17.057
	b_T (kJ/mol)	1.5294	1.7767	1.2541
	S.D.	0.4025	0.2927	1.2871
	R^2	0.9193	0.9714	0.8909
Dubinin-Radushkevich	Q_{DR} (mg/g)	6.3794	5.7096	11.734
	E (kJ/mol)	10.459	0.4793	4.2408
	S.D.	0.1329	0.1088	0.4221
	R^2	0.7425	0.9431	0.7518

Langmuir adsorption isotherm [29] describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent [30] and after that no further adsorption takes place [31].

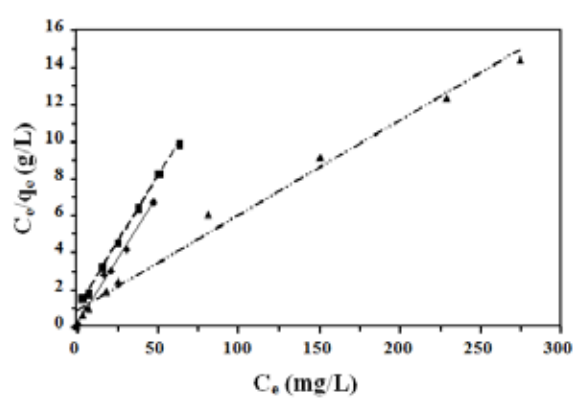

Figure 7. Langmuir isotherm model for RC (♦——), for AAC (■– – –) and for PCN (▲–··–·–).

Langmuir isotherm model assumes the mechanism of the adsorption process as a monolayer adsorption on completely homogeneous surfaces where interactions between adsorbed molecules are negligible [32].

Volume : 3 | Issue : 7 | July 2014 • ISSN No 2277 - 8179

Table 3. The RL values based on the Langmuir isotherm model for the adsorption of Cu^{2+} ions at different initial concentrations on the different types of clay:

RC		AAC		PCN	
C_o (mg/L)	$R_{L\ Value}$	C_o (mg/L)	$R_{L\ Value}$	C_o (mg/L)	$R_{L\ Value}$
42.86	0.0201	14.29	0.3259	15	0.5122
57.14	0.0152	28.57	0.1947	65	0.1951
71.43	0.0122	42.86	0.1388	80	0.1645
85.71	0.0102	57.14	0.1078	115	0.1204
100.00	0.0087	71.43	0.0882	130	0.1080
114.29	0.0076	85.71	0.0746	215	0.0682
128.57	0.0068	100.00	0.0646	315	0.0476

It can be noted in Table 4 that the R_L values decrease with the increase in the initial Cu^{2+} concentration indicating that the ion exchange is more favorable at higher initial concentration or in other words, by increasing the initial concentration the removal process became more favorable with assumption of Langmuir isotherm model.

Effect of temperature on the adsorption process:
As shown in figure (8), the change in adsorption capacity has the same behavior in case of RC and PCN. The removal capacity began with 6.02 and 10.43 mg/g for RC and PCN at 25 °C, respectively. The adsorption process increased by increasing the temperature which reached 7.45 and 12.91 mg/g at 70 °C, respectively.

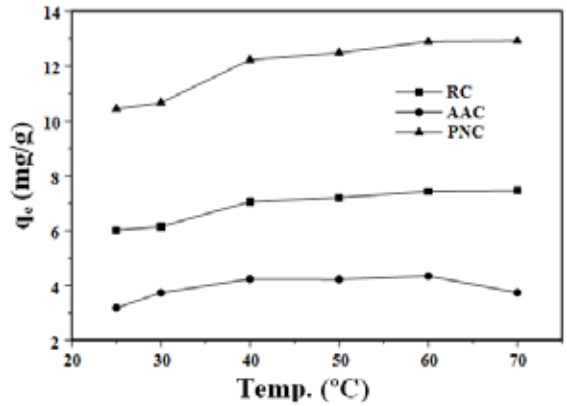

Figure 8. Effect of the temperature on the adsorption of Cu^{2+} ions on the different types of clay.

Conclusion:
The efficiency of RC, AAC and PCN was investigated for the removal of copper from aqueous solutions and wastewaters. XRD, TGA and IR analyses were used to characterize the mineralogical compositions of the adsorbents. Batch adsorption method was applied for optimization of adsorption conditions. Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich isotherm equations have been applied to analyze the obtained experimental data. RC and AAC were best fitted with Langmuir with correlation coefficients (R^2) of 0.9946 and 0.9989, respectively; while PCN was best fitted with Freundlich with R^2 = 0.9973.

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