Research Article

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Remediation of Copper and Zinc from wastewater by modified clay in Asir region southwest of Saudi Arabia

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Abstract: To investigate the efficacy of modified clay minerals to remediate heavy metals from industrial wastewater, two natural clay sediments dominated by kaolinite were selected. Since the kaolinite clay has low cation exchange capacity, some modifications were made using unusual treatments thermal transformation and acid activation techniques were used to increase exchangeability properties for producing modified kaolinite. The increased exchangeability was demonstrated through various methods. Results of X-Ray diffraction analysis verified the transformation of Kaolinite as indicated from disappearing all the diffractogram peaks due to kaolinite. In infra-red spectroscopy, the presence of a broad band with little change in the intensity in the region coupled with broad Si-O bending vibration band and Si-O-Al compound vibration bands explain the extent of structural disorder as a response of modification treatment. From a mineral structural viewpoint, destruction through heat treatment exposes directed –OH bonds located between the tetrahedral and octahedral layers (amorphization). It has been observed that after an acidification treatment, the –OH groups become less stable and lead to the newly formed vacant sites during the modification treatments accommodate extra structural water; thereby; broadening the –OH bands in the I.R spectrum.

Scanning Electron Microscope study has clearly demonstrated that, transformation in kaolinite structure from hexagonal original shape to edgeless shape and values of Cation Exchange Capacity C.E.C were increased from 8.2 to 18.41 Meq/100g and from 12.66 to 28.53 Meq/100g

in both Sinai and Aswan sediment, respectively. Result of the present study has indicated that crystalline structure of kaolinite transformed to collapsed structure after modification treatment and the new structure can absorb a large amount of pollutant metallic ions including Zn and Cu from wastewater.

Observed increase of metal ions removed by modified clays are due to increase of exchange sites produced by the acid leaching on a collapsed kaolinite framework. A comparison of relative removing values between Zn and Cu revealed that the removing kinetics of Cu is more favored under identical molar concentrations than Zn.

Keywords: Heavy metals removal, I.R spectroscopy, Modified kaolinite, S.E.M, Wastewater treatment

1 Introduction

As the world's population continues to grow, there are been a continuous rise in the demand for clean potable water. At the same time the availability and uncontaminated surface and ground water resources are not only limited but also exhausting at an alarming rate.

According to [1] deterioration of water quality was considered to be one of the seven most critical challenges of water.

Several techniques were employed to remove the contaminants and eliminate or reduce the pollutants and prepare the water for release into the environment safely. Most of these techniques required extensive handling of material and excessive time to achieve removal of solids, oils and metal ions from the water.

Currently, the most common used techniques make use of several types of techniques make use of several types of material that are used to adsorb wastewater contaminants; among these, clays were found to have remarkable affinity for heavy metal ions. Through ion exchange process the metal ions get bounded to the clays by electrostatic forces of attraction between the metal ions in solution and the anionic surfaces on the clay particles, [2, 3].

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Although Kaolinite clay mineral has least exchangeability properties, several researchers confirmed that modified kaolinite have potential ability to adsorb metal ions from solution [4–6].

A modified kaolinite amorphous derivative (metakaolinite $\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5$) which is produced from calcination of kaolinite at 600°C , absorbs heavy metals and could be used in the treatment of toxic metal pollution in water [7, 8]. [4, 9, 10] reported that the porous structure of collapsed modified kaolinite structure can adsorb a large amount of metallic ions such as Pb, Cd and Cu from wastewater. [11] reported that sodium-capturing capacity has been significantly increased, by applying modified kaolinite.

In the view of above, present study was conducted with a view to (i) develop modified kaolinite from local clay to increase its ion exchange capacity, and (ii) to compare the results for estimating the efficacy of modified clay over non-modified clay for remediation of heavy metals from the industrial wastewater.

2 Sampling and Preparation

2.1 Clay sediments

Two clay sediments samples were collected from both Aswan, South of western desert, Egypt and El Tih plateau, Sinai, Eastern desert, Egypt.

The clay was washed with distilled water to remove soluble impurities and wet sieved through 350 mesh sieve ($45\ \mu\text{m}$), homogenized and $<45\ \mu\text{m}$ fraction was collected. The clay then was reacted with $0.5\ \text{N}\ \text{Ca}(\text{NO}_3)_2$ and rinsed with distilled water to eliminate excess salts, [12].

Each clay sample was divided into two portions, the former was retained as a raw sample and the later portion was modified as follows:

Heating the clay sample to 600°C for 2 hrs. before subjecting to acid treatment by refluxing with $2\ \text{M}\ \text{HCl}$ at 80°C for 20 min. The sample was washed until free of chloride ions using double distilled water. Thus a set of 4 samples (two raw and two modified) was generated as follows:

Aswan kaolinite raw (Ar)

Aswan modified kaolinite (Am)

Sinai kaolinite raw (Sr)

Sinai modified kaolinite (Sm)

2.2 Wastewater

Industrial non-treated wastewater was collected from Abha industrial city, Iron and Steel small factory, Abha, south-west of Saudi Arabia. Wastewater samples were prepared according to [13] for both chemical analysis and heavy metals determination.

3 Analytical Methods

3.1 Physical and chemical analyses:

According to [14], various analyses of clay sediments were carried out as follows: particle size analyses (pipette method), calcium carbonate (volumetric calcimeter method), organic carbon (walkely and Black method), and cation exchange capacity (sodium saturation method). Determination of heavy metals in water were carried out by Inductive Coupled Plasma – Optical Emission (ICP-OES), whereas pH and EC were determined in water as well as clay sediments using glass electrode and electrical conductivity methods, respectively.

3.2 Mineralogical analyses

3.2.1 X-Ray Diffraction (XRD) analysis

A thin slurry of the sample solution was aliquot into a glass slide, air dried at room temperature and subjected to a Philips X-ray unit (PW 1830 fitted with a scintillation counter model PW 3020). The XRD analysis was done using Ni filter and $\text{Cu-K}\alpha$ radiation. At $\text{KV}=40$, $\text{MA}=20$, $\text{Gain}=60$, $\text{Range}=1000$, time constant during scans were 2, and chart drive $2\ \text{cm/min}$.

3.2.2 I.R spectroscopy

Infra red absorption spectra in region of $400\ \text{cm}^{-1}$ to $4000\ \text{cm}^{-1}$ were recorded using KBr sample pellets. The samples prepared as pellet method following the procedure of [15].

3.2.3 Scanning electron microscope (S.E.M)

The electron microscopy was performed in the Central Lab of Faculty of Agriculture Ain Shams University for Ar and Am clays after samples preparation according to [16].

Table 1: Some chemical properties of wastewater used (mg/L).

pH	EC ds/m	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	Fe	Ni	Cd	Zn	Cu	Pb
8.15	2.64	134	44	324	27.4	511	209.7	319.4	10	0.3	10.2	110	102	1.46

Table 2: Some physical and chemical properties of sediments used.

Clay sediments	EC ds/m	CaCO ₃ %	pH 1:2.5	O.C %	C.E.C meq/100g	Coarse Sand%	Fine Sand%	Silt %	Clay %	Textural Class
Aswan	1.01	8.21	8.1	0.02	12.66	3.35	6.44	18.67	71.54	Clay
Sinai	0.21	7.15	7.9	0.034	8.20	4.18	8.21	26.61	61.00	Clay

Figure 1: XRD analysis of raw and modified clay samples

3.3 Procedure of Heavy metals uptake

Fifty milliliters of non-treated Industrial wastewater was equilibrated with 0.5 gm clay sample for 5, 30, 60, 90, 120, 180 and 240 min. intervals. Initial pH was adjusted at 5.5 before starting the experiments. After centrifugation, the solution was analyzed for Cu and Zn using ICP-OES. Heavy metals released by clay minerals were calculated by the difference between initial concentration of the heavy metals and their concentration at equilibrium.

4 Results and Discussion

4.1 Chemical characterization of wastewater

Analytical results have indicated that the wastewater was alkaline as well as saline. In which, sodium and chlorine were dominant cation and anion respectively, Table 1.

The Copper, cadmium and zinc were the dominant contaminants in water.

4.2 Characterization of clay sediments

Table 2 summarised the observed physical and chemical characteristics of the sediments. Both locations are non-saline, non-calcareous, moderate alkaline and weak in organic carbon. Values of Cation Exchange Capacity (CEC) are related to clay content in each sediment.

4.2.1 XRD analysis

X-ray diffraction was carried out to identify the mineralogical composition of the used sediments and to study the changes after modification treatments. Obtained diffraction patterns were illustrated in Figure 1. The results re-

Figure 2: LR Spectra of raw and modified clay samples

vealed that the kaolinite is predominant in both used sediments. This could be noted from the intensity peaks at 7.13, 4.64, 3.83, 3.56, 2.73, 1.66 and 1.48 Å. Besides, quartz is also presents in the two sediments as indicated by the peak at 3.34, 1.82 and 1.54 Å.

After modification process, all the peaks in the diffractograms indicating kaolinite were disappeared, indicating its transformation to modified kaolinite. On the other hand the diffraction patterns caused did not change indicating relative stability of quartz during treatments.

4.2.2 Infra-red absorption spectrometry

To ensure the mineralogical composition of raw and modified clays, infra-red analysis spectroscopic study of the samples was carried out. The results of this study are shown in Figure 2, and the band assignments has been provided in Table 3. The raw sediments have exhibited all the characteristic bands of both kaolinite and quartz indicated by 3696, 3621, 913, 754 cm^{-1} and 793, 694 cm^{-1} , respectively, [15]. The band at 3654 cm^{-1} indicated that kaolinite shows disorder form. On the other hand, the modified clays show following differences;

Table 3: Band assignments of kaolinite sediments.

Wavelength (cm^{-1})	Assignments	References
~3700	OH stretching hydroxyl sheet	[9]
3620	Inner OH stretching vibration	[9]
1114 – 1034 - 1008	Si-O bending vibration	[11]
913	Al-OH bending	[9]
753 and 540	Si-O-Al compound vibration	[11]
797 - 697	Silica, quartz	[9]

Figure 3: Ideal structure of kaolinite mineral

- (1) The Absence of vibration band at 913 cm^{-1} indicating breaking of Al-OH bonds and increasing availability of $-\text{OH}$ groups in the structure.
- (2) The persistence of 1008, 1034, 1114 cm^{-1} band indicating presence of Si-O bonds in the structure.

As the result of modification treatment the disordered kaolinite structure was shown in the region of Si-O and Si-O-Al bands with change in the intensity. From a mineral structural viewpoint, destruction through heat treatment exposes directed $-\text{OH}$ bonds located between the tetrahedral and octahedral layers (amorphization) Figure 3. After acidification treatment, the $-\text{OH}$ groups become less stable. The newly formed vacant sites during the modification treatments accommodate extra structural water; thereby; broadening the $-\text{OH}$ bands in the I.R spectrum, [17] confirmed the same interpretation.

Table 4: Cation exchange capacity (Meq/100g) of raw and modified clays

Clay sediments	Sr	Sm	Ar	Am
C.E.C	8.20	18.41	12.66	28.53

4.2.3 Scanning Electron Microscope (SEM)

The scanning electron microscopic study was carried out for both raw and modified Aswan clay samples, Figure 4(a).

The presence of hexagonal shape particles with clear edges confirmed the presence of kaolinite in unmodified clay sample Figure 4(a). After modification treatments, transformation in kaolinite structure was observed from hexagonal shape to edgeless shape Figure 4(b). The shapes are more pronounced at the higher magnification see, Figure 4(c).

4.3 Cation Exchange Capacity

In order to assess the exchangeability of clay samples after modification treatments, C.E.C values were measured for raw and modified clay samples, which are shown in Table 4. The modification treatments nearly, duplicated the C.E.C values in the clay samples, which shows remarkable change from 8.2 to 18.41 Meq/100g and from 12.66 to 28.53 Meq/100g in Sinai and Aswan sediments, respectively.

The obtained results are similar to those published by [12] who reported four-fold increase in CEC values after the thermal treatment at 600°C followed by acid activation treatment of the samples.

The observed increase in C.E.C after modification treatments is indicative of the increasing number of exchangeable sites caused during the modification treatments. Acid attack cleans up the mineral by leaching of metal ions from collapsed lattice structure due to the disorder caused by the transition of kaolinite to metakaolinite by using thermal treatment. In this respect, [18] has mentioned that unless a little surface change was observed on calcining kaolinite to less than 550°C , a marked change in the exchange kinetics can not be expected.

4.4 Heavy metals uptake

The effect of equilibration time on the sorption of copper and zinc was analyzed kinetically over a range of 0-240 min. From theoretical point of view, adsorption process requires long equilibration time, while the practical

Figure 4: Scanning electron microscope of Aswan raw and modified clay sediment

Figure 5: Amount of heavy metals removed (mg/g) by raw and modified clay

approach needs a short contact time, this in accordance with [19]. The removing kinetics of Cu and Zn ions by raw and modified clay samples were monitored as a function of equilibration time and plotted in Figure 5. All metal ions attain a near equilibrium condition within the first 90 minutes and attains near-complete removal in about 2 hrs time.

The obtained results indicate that the modified clay sample have rendered maximum ion removal [2.78(Cu) and 2.00 (Zn) mg/g] for Sm clay; representing about [27.25% and 18.18%] from initial wastewater concentration, respectively.

Besides, 3.38(Cu) and 2.44(Zn) mg/g for Am clay represents about 33.14% and 22.18% from initial wastewater concentration, respectively. The observed increase of removed metal ions by modified clays are due to the increasing ex-

change sites produced after acid leaching on a collapsed kaolinite structure.

A comparison of relative removing values in Figures 5 has revealed that the removing kinetics of copper are more favored under identical molar concentrations than zinc.

This may be due to the formation of $\text{Cu}(\text{OH})^+$ and $\text{Cu}(\text{H}_2\text{O}_4)^{2+}$ complex which can stabilize copper ions. It was also suggested that Cu^{2+} ions largely occupy the planar external surface rather than the edges of platelets. Moreover, zinc can form comparatively stable chloride complexes in solution which might not get re-adsorbed resulting into lower sorption kinetics for Zn as compared to Cu.

Several studies such as [20, 21]. Have confirmed previous finding. For e.g. [21] have shown that higher surface

charge is the more selective for exchange process in favor of Cu with respect to Zn.

Also, [22] studied Laterite adsorbent and concluded the this sorpment can be preferred for removal of copper confirming the prsent finding.

However, on the contrary, [23] have observed that zinc is better removed than cobber by expanded vermiculite. The authors argued about the selectivity of zinc to get adsorped in the expanded vermiculite structure than copper. Nevertheless, a recent study carried out by [24] found that Verde-Iodo clay presented higher affinity and selectivity for copper than silver. So, each clay type have their own selectivity toward specific heavy metals.

Clay sediments interact with heavy metals through a variety of mechanisms. The dominating type of bond depends on the metal, the type of binding sites, the access to these binding sites and a variety of geochemical environment. The main mechanisms for retention of heavy metals in clay minerals include adsorption, ion exchange, precipitation and co-precipitation; [5].

The present study has indicated that the ion exchange might be the probable mechanism of Cu and Zn ions uptake by modified kaolinite clays. Besides, a possibility that the metal ions being entrapped into the pores cannot be ruled out.

5 Conclusions

To produce a new modified clay as a sorbent for removing heavy metals and other toxicants from industrial wastewater, two Egyptian natural clay sediments dominated mainly by kaolinite were selected from Aswan and Sinai regions. Unusual treatments depended upon thermal transformation and acid activation were carried out to increase the exchangeability properties of kaolinite and produce modified kaolinite. This was proved by a variety of methods, including XRD analysis, IR spectroscopy, SEM study and C.E.C measurements.

The results of present study have indicated uptake of heavy metals by modified clay samples indicating that the Sinai have rendered maximum ion removing about (27.25% and 18.18%) from (Cu) and (Zn) respectively. Beside, 33.14% (Cu) and 22.18% (Zn) for Aswan modified clay from initial wastewater concentration. It has been indicated that the removing kinetics of Cu are more favored under identical molar concentrations than that of Zn. This may be due to the formation of $\text{Cu}(\text{OH})^+$ and $\text{Cu}(\text{H}_2\text{O}_4)^{2+}$ which can stabilize copper ions. It was also suggested that Cu^{2+} ions largely occupy the planar external surface rather

than the edges of platelets. Moreover, zinc can form comparatively stable chloride complex in solution which will not get re-adsorbed after getting desorbed into the solution due to the prevailing conditions. This explains the observed lower sorption kinetics for Zn as compared to Cu.

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References

- [1] Abu-zeid, M., Water in Africa and future challenges. The 18th congress of the international commission an irrigation and drainage, Montreal, Canada, 2002 July 21-28.
- [2] Pierluigi B., Francesca L., Ion Exchange Resins: Catalyst Recovery and Recycle. Chem. Rev., 2009, 109 (2), 515-529 DOI: 10.1021/cr800404j <https://pdfs.semanticscholar.org/b196/1f523b5538d5a32698147094c4bc8327a944.pdf>
- [3] Mazzoldi P., Carturan S., Quaranta A., C. Sada S., Sglavo V. M., Ion Exchange Process: History, Evolution and Applications. La Rivista del Nuovo Cimento 2013, 36(9), 397-460 DOI 10.1393/ncr/i2013-10092-1
- [4] Miranda-Trevino J. C., Coles C. A., Kaolinite properties, structure and influence of metal retention on PH. Appl. Clay Sci. 2003, 23,133-139. [https://doi.org/10.1016/S0169-1317\(03\)00095-4](https://doi.org/10.1016/S0169-1317(03)00095-4)
- [5] O'Day P. A., Parks G. A., Brown G. E., Molecular structure and binding sites of cobalt (II) surface complex on kaolinite from X-ray absorption spectroscopy. Clays & clay mineral, 1994,42, 337-355. DOI: 10.1346/CCMN.1994.0420312
- [6] Sari A., Tuzen M., Cd (II) adsorption from aqueous solution by raw and modified kaolinite. Appl Clay Sci., 2014, 88, 63-72 <https://doi.org/10.1016/j.clay.2013.12.021>
- [7] Kakali G., Perraki T., Tsvilis S., Badogiannis E., Thermal treatment of Kaolin: the effect of mineralogy on the pozzolanic activity. Appl. Clay Sci. 2001, 20, 73-80. [https://doi.org/10.1016/S0169-1317\(01\)00040-0](https://doi.org/10.1016/S0169-1317(01)00040-0)
- [8] Murray H. H., Traditional and new applications for kaolin, smectite and playgorskite: a general overview. Appl. Clay sci. 2000, 17, 207-221 [https://doi.org/10.1016/S0169-1317\(00\)00016-8](https://doi.org/10.1016/S0169-1317(00)00016-8)
- [9] Coles C. A., Yong R. N., Aspects of kaolinite characterization and retention of Pb and Cd. Appl. Clay Sci. 2002, 22, 39-45. <https://pdfs.semanticscholar.org/0a67/90d14853df562568cd6ceaa17689cf08a55d.pdf>
- [10] Bhattacharyya K.G., Gupta S. S., Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review. Adv. Colloid Interface Sci. 2008, 140(2), 114-31. doi: 10.1016/j.cis.2007.12.
- [11] Xiuju Zhang, Huan Liu, Haoxuan Xing, Halyan Li, Hong Jun Hu, Aijun Li, hong Yao, Improved sodium adsorption by modified kaolinite at high temperature using intercalation-exfoliation method. Fuel, 2017, 191, 198-203. <https://doi.org/10.1016/j.fuel.2016.11.067>
- [12] Suraj G., Iyer, G. S. P., Ialithambika, M., Adsorption of cadmium and copper by modified kaolinites. Appl. Clay Sci., 1998, 13, 293-

- 306 [https://doi.org/10.1016/S0169-1317\(98\)00043-X](https://doi.org/10.1016/S0169-1317(98)00043-X)
- [13] Greenberg A. E., Clesceri L. S., Eaton A. D., Standard methods for the examination of water and wastewater. Published by American public health association, American Water Works Association, Water Environment Federation 1992 https://www.mwa.co.th/download/file_upload/SMWW_1000-3000.pdf
- [14] Black C. A., Evans D. D., Ensminger L. E., White J. L., Clark F. E., Methods of Soil Analysis. American Society of Agronomy, Inc., Madison, Wisconsin, USA Library of Congress Catalog Card Number: 1985, 65-15 8 00, Seventh printing.
- [15] Russell J. D., Fraser A. R., Infrared methods. Chapter (2), pp: 11-67. In: Clay mineralogy: spectroscopic and chemical determinative methods. Wilson, M. J. (ed) Chapman & Hall, London. UK. Congress Catalog card no. 1994, 93, 74207. DOI: 10.1007/978-94-011-0727-3_7
- [16] Kittrick J. A., Electron Microscope Techniques. Chapter (47), pp: 1985, 632-651. In : Methods of Soil Analysis. Black et al. (ed.) Am. Soc. Agro., Madison, Wisconsin, U.S.A.
- [17] Suraj G., Lyer G. S. P., Rugmini S., Lalithambika M., The effect of micronization on kaolinites and their sorption behavior. Appl. Clay Sci. 1997, 12, 111-130. [https://doi.org/10.1016/S0169-1317\(96\)00044-0](https://doi.org/10.1016/S0169-1317(96)00044-0)
- [18] Abd-Allah, S. M., Probability of kaolinization of montmorillonite under certain soil conditions of Egypt. Annals Agric. Sci., Ain Shams Univ., Cairo, Egypt 2000, 45, 363-383.
- [19] Sdiri A. T., Higashi T., Jamoussi F., Adsorption of copper and zinc onto natural clay in single and binary systems. Int. J. Environ. Sci. Technol. 2014 11, 1081–1092 <http://doi.10.1007/s13762-013-0305-1> <http://www.bioline.org.br/pdf?st14107>
- [20] Vengris T., Brinkiene R., Sveikauskaite A., Nickel, copper and zinc removal from waste water by a modified clay sorbent. Appl. clay Sci. 2001, 18, 183 – 190. [https://doi.org/10.1016/S0169-1317\(00\)00036-3](https://doi.org/10.1016/S0169-1317(00)00036-3)
- [21] Susane Gier, William D. J., Heavy metal adsorption on micas and clay minerals studied by X-ray photoelectron spectroscopy. Appl. Clay Sci. 2000, 16, 289-299. [https://doi.org/10.1016/S0169-1317\(00\)00004-1](https://doi.org/10.1016/S0169-1317(00)00004-1)
- [22] Sudha Rani K., Srinivasb B., Gouru Naiduc K., Ramesha K. V., Removal of copper by adsorption on treated laterite. Materials Today: Proceedings 2018, 5, 463–469. <https://doi.org/10.1016/j.matpr.2017.11.106> <https://www.sciencedirect.com/science/article/pii/S2214785317323441>
- [23] Emanuelle Dantas de Freitas, Hewellyn Joacy de Almeida, Gurgel Adeodato Vieira, Binary adsorption of zinc and copper on expanded vermiculite using a fixed bed column, Appl. Clay Sci. 2017, 146, 503-509. <https://doi.org/10.1016/j.clay.2017.07.004> <https://www.sciencedirect.com/science/article/pii/S0169131717302971>
- [24] Emanuelle Dantas de Freitas, Hewellyn Joacyde Almeida, Ambrosio Florenciode Almeida Neto and Melissa Gurgel Adeodato Vieira, Continuous adsorption of silver and copper by Verde-lodo bentonite in a fixed bed flow-through column. J. Cleaner prod., 2018, 171, 613-621. <https://doi.org/10.1016/j.jclepro.2017.10.036> <https://www.sciencedirect.com/science/article/pii/S0959652617323272>