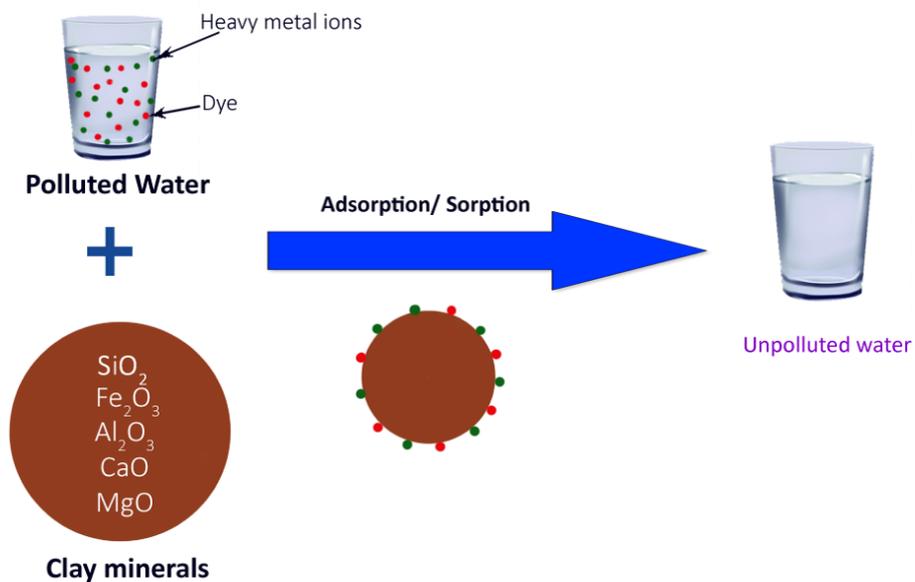


Removal of Congo red dye and Cd(II) and Fe(III) ions from aqueous solutions using clay minerals: Equilibrium adsorption studies

Y.M.L. Chaturangani and K. Masilamani*



Highlights

- Acid activation was performed on two types of locally available clays.
- Two types of acid activated local clays were used to remove the dyes from the aqueous solutions.
- The adsorption isotherms of these systems were studied using Langmuir and Freundlich isotherms.

RESEARCH ARTICLE

Removal of Congo red dye and Cd(II) and Fe(III) ions from aqueous solution using clay minerals: Equilibrium adsorption studies

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Abstract: This study was performed to assess the removal of dyes and heavy metals from wastewater using locally available natural clays. Modifications of two different local raw clays were carried out by acid activation. The characterization of the raw clay and modified clays were performed by FTIR spectroscopy. The effect of contact time, initial concentration of adsorbate, and temperature on the removal of Congo red (CR), Cd(II) and Fe(III) ions from aqueous solutions were investigated using the raw and acid-activated clays. The results showed that optimum adsorption efficiencies of these adsorbates were obtained in 24 h of contact time, for 400 mg L⁻¹ concentration of adsorbate at the temperature of 303 K. Acid activation of these clays increased the removal efficiency of CR from 80% to 90%, whereas 75% of Cd(II) and Fe(III) ions were adsorbed from aqueous solution by these raw clay minerals. The adsorption process of these systems was studied using Langmuir and Freundlich isotherms. The Langmuir adsorption isotherm gives a better fit for CR, Fe(III) and Cd(II) ions adsorption by the two types of raw clays, whereas CR adsorption by acid-activated clays shows a better fit to Freundlich isotherm. These clays can be used as a cost-effective adsorbent for the removal of pollutants from wastewater.

Keywords: Clay; heavy metals adsorption; dye adsorption; adsorption isotherm; water purification.

INTRODUCTION

Water is one of the essential components for the survival of all living beings. However, aquatic pollution is a huge environmental issue causing serious problems to living beings. Water is polluted in various ways by a wide variety of substances, such as toxic chemicals, sediments, plant nutrients, pathogenic microorganisms, organic waste, heat, petroleum (oil), and radioactive substances (Laws, 2018; Schweitzer *et al.*, 2018). These pollutants are released to the water bodies from various sources. Heavy metals and organic pollutants are mainly discharged to the water bodies by industries and these pollutants have become a major problem in the world (Siddique *et al.*, 2020). Organic dyes and Cd(II) and Fe(III) ions are commonly found in the aquatic systems which are closed to the industries. Cadmium has caught growing attention because of its bioaccumulation and pathogenicity and is one of the most toxic metal pollutants which can cause many serious diseases, such as renal dysfunction, calcium metabolism

disorders, prostate cancer, etc. (Friberg *et al.*, 1992, Satarug *et al.*, 2003; Komatsu *et al.*, 2007). On the other hand, the accumulation of Fe(III) and Cd(III) ions in the body can cause hereditary haemochromatosis which is a genetic disorder in the body. Therefore, it is important to note that the World Health Organization (WHO) prescribes the permissible limits for substances present in the drinkable water. According to the WHO standards, the permissible limits for Cd(II) and for Fe(III)/Fe(II) ions in drinking water are 0.003 mg L⁻¹ and 0.200 mg L⁻¹ respectively (Uddin *et al.*, 2017). Moreover, the WHO prescribes the permissible limit as 1.00 µg L⁻¹ for the coloring substances in drinking water (Allègre *et al.*, 2006). Therefore, the excess of these substances in the water has to be removed to make the water be consumed by the living organisms. Therefore, it is important to develop mechanisms to remove the organic pollutants and heavy metals from the aquatic systems. There are several methods such as membrane separation, electrocoagulation, reverse osmosis, flocculation, and adsorption have been used to remove heavy metals and organic materials from the aqueous medium (Ricart *et al.*, 2008; Toor *et al.*, 2018; Han *et al.*, 2019). Among these methods, the adsorption technique has been extensively used by many researchers to remove the organic and inorganic pollutants, since it has significant advantages over other techniques, such as low cost, ease of operation, and high effectiveness as well. Currently, different types of adsorbents such as activated carbon, chitosan, fly-ash, and clay minerals have been used for wastewater treatment (Ali *et al.*, 2012; Karnib *et al.*, 2014; Momina *et al.*, 2018). Among these adsorbates, varieties of clay minerals such as sepiolite, kaolinite, smectite, montmorillonite, bentonite, and zeolite have been investigated and used as low-cost adsorbate/minerals for the removal of these pollutants (Srinivasan, 2011; Kausar *et al.*, 2018). Clay minerals are hydrous aluminosilicate with very fine particle size and they have extensively been used as adsorbents for water purification due to their high cation exchange, swelling properties, and high surface areas (Parker *et al.*, 1982; Polubesova *et al.*, 2005). A few works have been reported to remove the organic and inorganic contaminants using activated clay from the water (Sennour *et al.*, 2009; Toor *et al.*, 2018; Taher *et al.*, 2019; Ayub *et al.*, 2020; Khalfa *et al.*, 2021).

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In this work, locally available raw clay and its acid-activated materials were employed in the removal of organic dye (Congo red) and heavy metals [Cd(II) and Fe(III) ions] from the aqueous media. The acid activation of the clay improve the removal efficiency of CR from 80% to 90%, whereas 75% of Cd(II) and Fe(III) ions were adsorbed from aqueous solution by these raw clay minerals. The adsorption isotherm studies were performed in these clay mineral systems using different isotherm models and the results show that the Langmuir adsorption isotherm gives a better fit for CR, Fe(III) and Cd(II) ions adsorption by the two types of raw clays, whereas CR adsorption by acid-activated clays shows a better fit to Freundlich isotherm.

MATERIALS AND METHODS

Materials

Solutions of Cd(II) and Fe(III) ions were prepared from CdCl₂ (99%) and FeCl₃·7H₂O (99%), respectively, and these salts were purchased from Sigma-Aldrich. Nitric acid and ammonium hydroxide were used to adjust the pH of these metal ion solutions and they were supplied by Sigma-Aldrich. All chemicals used for this research were analytical grade and used directly without further purification. All samples were prepared at room temperature (30 °C). Doubled distilled water was used for all experiments carried out in this research. The clay minerals were collected from two different places called Siththandy (GPS location: 7.82133, 81.549468) and Kommathurai (GPS location: 7.792986, 81.577418) in the Batticaloa district. These clays are kaolinite types of clays and were collected at 2.5 ft depth from the ground surface. These two types of clays are black in colour and are washed and dried before using them for adsorption studies.

Instruments

UV - Visible absorbance of samples was performed using a Biobase D580 series double-beam UV-visible spectrophotometer with the slit width and spectral bandwidth of 1.0 nm. All the measurements were made in a quartz cuvette with two clear windows using a path length of 1 cm. The absorbance of samples was recorded between the wavelength of 200 nm and 800 nm. All the pH measurements were carried out on a Mettler-Toledo Delta 320 pH meter. Fourier Transform Infrared (FT-IR) spectra were recorded in the range 4000 - 400 cm⁻¹ using a Bruker Vertex 80 FT-IR spectrophotometer. The sample was placed on the diamond crystal plate, and the spectrum was recorded in ATR mode. The concentrations of metal ions were recorded using a SensAA Dual GBC Scientific Equipment BK-D580 Atomic Absorption Spectrophotometer.

Acid activation of clay

The acid activation of clay was carried out at room temperature of 30 °C in a rotary shaker with an agitation control. Raw clay was treated with 0.2 M of HCl at 30 °C. The clay to acid ratio was fixed at 1:10 and was agitated using an orbital shaker at 200 rpm for 3 h for the acid activation. Then the acidified clay is separated from the solution and washed several times using a centrifuge

to remove the excess acid from the clay. The supernatant was collected from the centrifuge in each wash and Cl⁻ ions present in the supernatant were detected using a silver acetate solution. This washing process was performed until the supernatant was free from Cl⁻ ions. Then the acidified clay was dried in an oven at 55 °C for 12 h and stored in an air-tight plastic bottle for further use.

Preparation of metal ion solutions

Solutions of Cd(II) and Fe(III) ions concentrations varying from 100 mg L⁻¹ to 400 mg L⁻¹ were prepared by dissolving their respective metal salts (CdCl₂ and FeCl₃) in 500 mL distilled water. The pH of the solutions was adjusted using nitric acid and ammonium hydroxide to avoid the precipitation of metal ions and the pH of all solutions of metal ions was maintained at around 4.5.

Batch adsorption test of heavy metals and dye (CR) on the clay

The adsorption of the above-mentioned metal ions and CR by the adsorbents was studied through batch experiments. Clay samples (0.5 g) were added into 50 mL of different concentrations of Cd(II), Fe(III) ions and CR solutions (100, 200, 300, and 400 mg L⁻¹) separately at 30 °C and were stirred at constant stirring at 200 rpm for different equilibrium times (4 h, 6 h, 12 h, and 24 h). After the equilibrium was reached, the solid and liquid phases were separated using a centrifuge. The initial and the final metal ion concentrations were determined by atomic adsorption spectrophotometer (AAS) and the removal percentages of the heavy metal ions were estimated. The absorption measurements were recorded at the wavelengths of 228.8 nm, 340 nm using AAS for Cd(II) ions, Fe(III) ions respectively, and CR at 500 nm using a UV-visible spectrophotometer. All the adsorption studies were performed three times.

The study of adsorption isotherms was performed for metal ions and CR adsorption on clay samples using concentrations from 100 to 400 mg L⁻¹.

The removal percentages of the dye and heavy metal ions using different local clays were estimated by the following equation,

$$\text{Removal (\%)} = \frac{C_i - C_e}{C_i} \times 100$$

where C_i is the initial concentration (ppm) and C_e is the concentration at the final equilibrium (ppm). The data from the triplicate experiments varied within 4%.

Adsorption data for different adsorbate concentrations are described by Langmuir and Freundlich as adsorption isotherms.

The Langmuir model is given by the following equation;

$$\frac{C_e}{q_e} = \frac{1}{Q_m C_L} + \frac{1}{Q_m} C_e$$

where C_e is the equilibrium concentration of the adsorbate (mg L⁻¹), q_e is the amount of adsorbate adsorbed per unit of clay (mg), Q_m the Langmuir constant for adsorption

capacity (mg g^{-1}) and K_L is the Langmuir constant for the energy of adsorption (L g^{-1}).

The Freundlich model is applicable to heterogeneous systems and involves the formation of multilayers. The Freundlich adsorption isotherm is given by:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e$$

where, K_f and n are Freundlich constants that correspond to adsorption capacity and adsorption intensity, respectively. Freundlich equilibrium constants were determined from the plot of $\ln q_e$ versus $\ln C_e$.

RESULTS AND DISCUSSION

Acid activation of clay

In this work, the clay minerals were undergone acid activation to improve their adsorption capacity against the CR. Acid activation is a technique that is used for the modification of clay minerals. The purpose of acidification of the clay is to improve the adsorptive properties, surface crystallinity, surface functionalities, specific surface area, and selectivity for different adsorbates. This acid activation provides rich acidic nature in the octahedral sheet of the clay. This acid activation mechanism occurred through the substitution of exchangeable cations such as Al(III), Mg(II), and Fe(II) ions in the octahedral sheet against the protons. This phenomenon improves the bleaching and adsorption efficiencies, increases the porosity and the specific surface area of the materials, and provides a high affinity towards the organic molecules (Vimonses, 2011).

Characterization of clays

FT-IR analysis

The FT-IR spectra of Kommathurai (K) and Siththandy (S) clays (raw and acid-activated clay) are shown in Figure 1 and Figure 2 respectively. The FT-IR spectra of both of the raw and acid-activated clays (K clay and S clay) show the presence of Al-OH as stretching bands at 3622 cm^{-1} and as its bending bands at 910 cm^{-1} . The intensities of these

peaks are slightly increased after the acid activation of clay. The broadband centered near 3408 cm^{-1} for K clay and 3412 cm^{-1} for S clay are due to the -OH stretching mode of the interlayer water. The absorption band in the region of $1626 - 1627 \text{ cm}^{-1}$ is assigned to the -OH bending mode of adsorbed water (Fill *et al.*, 2014). The absorption band at 1028 cm^{-1} corresponds to the Si-O-Si and Si-O stretching vibration (Oubagaranadin *et al.*, 2010). Moreover, the Si-O stretching vibrations were observed at about 775 cm^{-1} and this shows the presence of quartz in the clay (Borchardt, 1977).

Adsorption studies

Effect of contact time on the adsorption

Contact time is one of the most effective factors in the batch adsorption process. Therefore, the effect of contact time on various clays over the dye and metal ions [Cd(II) and Fe(III) ions] were investigated and the results are shown in Figure 3 and Figure 4 respectively. The adsorption rate initially increased rapidly, and the optimal removal efficiency was reached within about 24 h. This result shows that the adsorption efficiency tends to increase with time of contact and this is because the number of vacant sites in the adsorbent keeps on decreasing with the time during the adsorption process and the adsorbate gets adsorbed until saturation is reached. Therefore, the dye and the metal ions solutions were kept contacted for 24 h with adsorbent in all analyses.

Effect of initial adsorbate concentration on the adsorption

The effects of the concentration of CR and metal ions [Cd(II) and Fe(III) ions] on the adsorption efficiency of different clay minerals were investigated and the outcomes are shown in Figure 5 and Figure 6 respectively. This reveals that the adsorption efficiency of these adsorbents was increased with an increase in adsorbate dose and the optimum adsorption efficiency was obtained at 400 mg L^{-1} . This revealed that the adsorption reaction increases until the adsorption sites in the adsorbates are saturated and the optimum adsorption efficiency occurs when all the

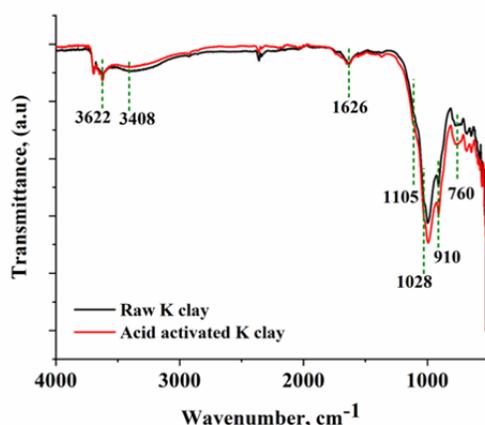


Figure 1: FT-IR spectra of raw and acid-activated Kommathurai (K) clay.

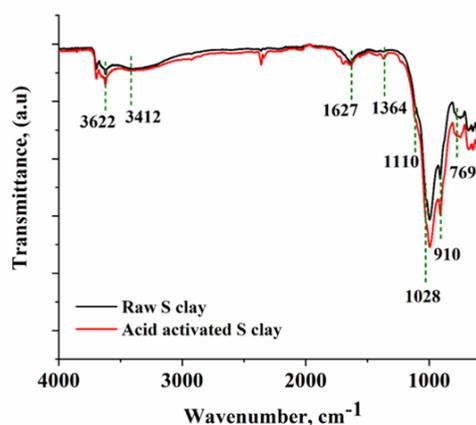


Figure 2: FT-IR spectra of raw and acid-activated Siththandy (S) clay.

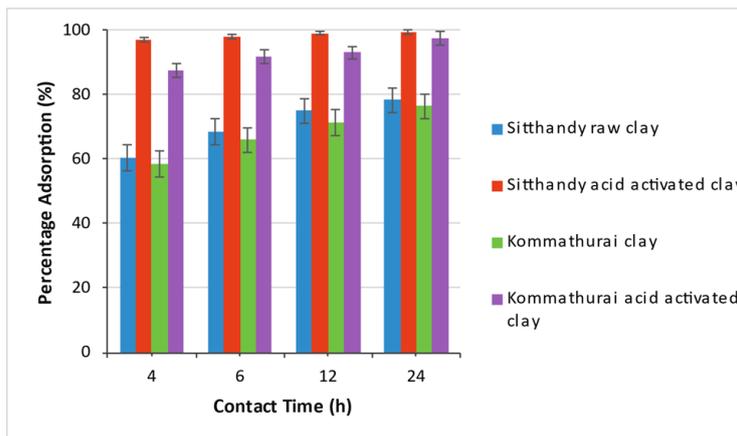


Figure 3: Effect of contact time on adsorption of CR by different clays (Initial dye concentration 400 mg L⁻¹).

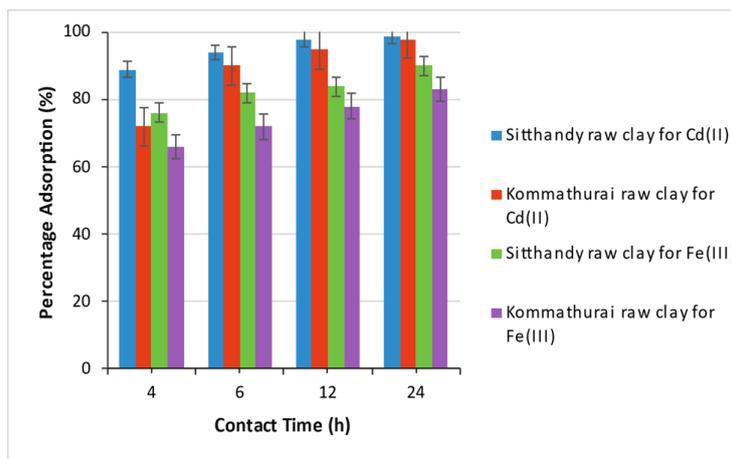


Figure 4: Effect of contact time on adsorption of different heavy metal ions (Initial metal ions concentrations 100 mg L⁻¹).

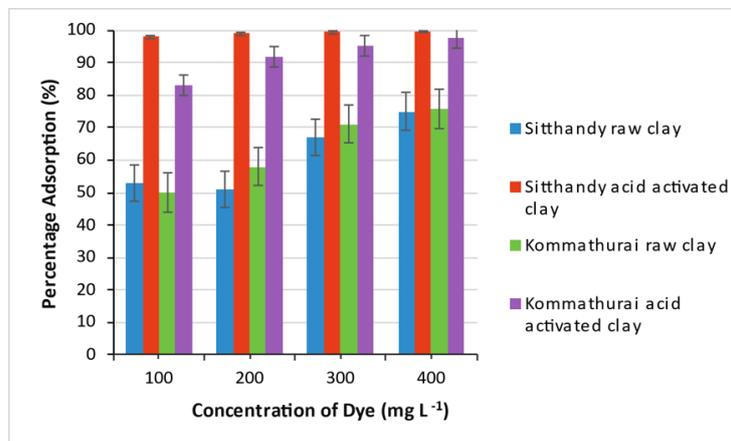


Figure 5: Effect of initial dye concentration on adsorption of Congo red by different clays (Contact time: 24 h).

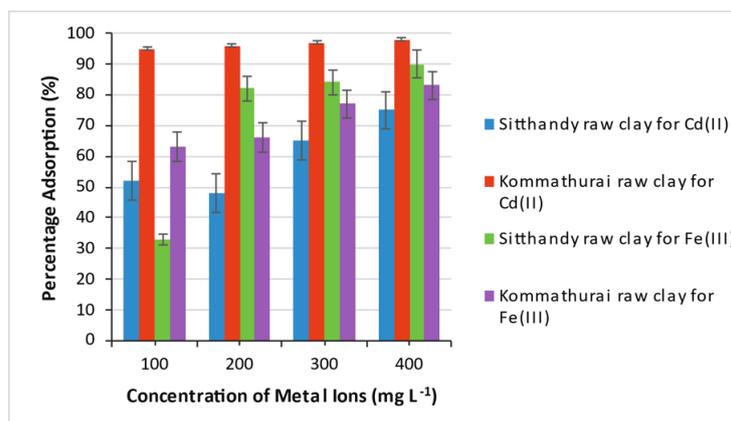


Figure 6: Effect of initial concentration of heavy metal ions on adsorption by different clays. (Contact time: 24 h).

adsorption sites are saturated. Therefore, 400 mg L⁻¹ of these adsorbates was considered as the optimum and they are used for further analytical studies.

Effect of temperature on the adsorption

The temperature is one of the important parameters that affect the adsorption efficacy. Therefore, the effect of temperature on the adsorption of the CR and metal ions [Cd(II) and Fe(III) ions] onto different clays were studied by conducting different sets of experiments at different temperatures such as 293, 298, 303, and 308 K. It was observed that adsorption of metal ions increases with the increase in the temperature. However, the measurement of adsorption was recorded at the temperature of 303 K.

Equilibrium adsorption studies

It is important to understand the distribution of adsorbate between the solid and liquid phases at equilibrium and this can be investigated through adsorption isotherms. These isotherms describe the interaction of adsorbate with the adsorbent, including the adsorption types and features. Generally, there are two types of models used to study the adsorption mechanism and those are Langmuir isotherm and Freundlich isotherm. In this work, both Langmuir and Freundlich isotherm models were used to evaluate the adsorption mechanism.

Langmuir adsorption isotherm

In the Langmuir model, maximum adsorption is achieved when a monolayer of adsorbate covers the adsorption surface. This model assumes that constant adsorption energy and independent of surface coverage during the adsorption process. Moreover, this also assumes that the adsorbent surface is homogeneous in character and possesses identical and energetically equivalent adsorption sites.

The Langmuir adsorption isotherm study was carried out from the data obtained in the adsorption of CR using the raw and acid-activated clays and the data from the adsorption of metal ions such as Cd(II) and Fe(III) ions by the raw clays. In this model, the q_m and K_L values were obtained from the slopes and intercepts of their respective linear plots of C_e/q_e versus C_e , and the results are shown in Table 1 and Table 2. These results show that the adsorption of CR, by Siththandy raw clay was well-fitted to the Langmuir model than the Kommathurai clay. Moreover, the adsorption of Cd(II) and Fe(III) ions by the raw clays was not well-fitted to the Langmuir adsorption isotherm model based on their respective correlation coefficient, R^2 as listed in Tables 1 and 2.

The favorability and feasibility of the adsorption process can be determined by the separation factor R_L in the analysis from Langmuir isotherm and it is given by the following equation.

$$R_L = \frac{1}{1 + K_L C_i}$$

where the K_L is the Langmuir constant for the energy of adsorption (L g⁻¹) and C_i is the initial dye concentration (mg L⁻¹).

The slope of the isotherm depends on the value of R_L as follows: The isotherm is unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [Tan *et al.*, 2009]. Figures 7 and 8 demonstrate the changes in separation factor, R_L with initial concentrations of dye, and heavy metals for various adsorbents. In the present study, the value of R_L in all cases lies between 0 and 1 indicating that the dye adsorption is favourable by both raw and acid-modified local clays and the adsorption of heavy metals is favourable by raw clays.

Table 1: Langmuir adsorption isotherm constants for CR adsorption.

Adsorbent	q_m	K_L	R^2
Raw Siththandy clay	3.79075	0.07384	0.9925
Acid Activated Siththandy clay	6.4143	0.07142	0.8716
Raw Kommadurai clay	7.01754	0.008193	0.8823
Acid Activated Kommadurai clay	16.3666	0.19046	0.7049

Table 2: Langmuir adsorption isotherm constants for Cd(II) ions and Fe(III) ions adsorption.

Adsorbent	q_m		K_L		R^2	
	Cd(II)	Fe(III)	Cd(II)	Fe(III)	Cd(II)	Fe(III)
Raw Siththandy clay	3.9323	0.70042	2.0007	9.9699	0.9765	0.9813
Raw Kommathurai clay	3.03859	2.1838	1.8902	0.4390	0.8808	0.9656

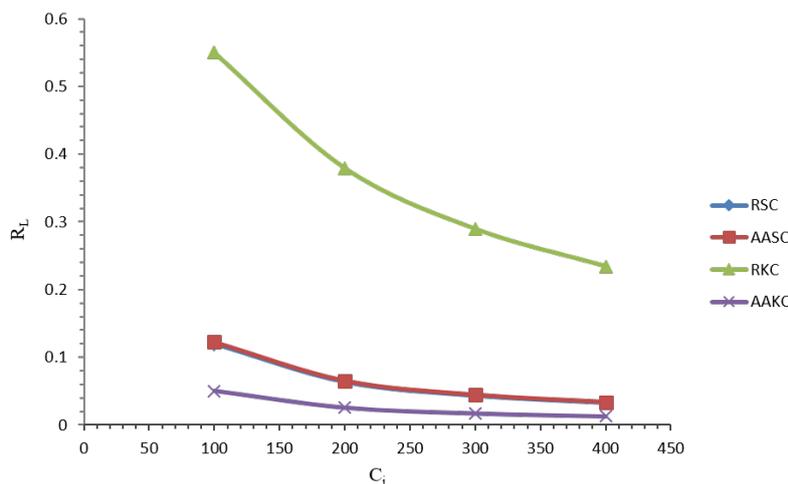


Figure 7: Effect of initial CR concentration on the separation factor, R_L : (RSC-Raw Siththandy Clay, AASC- Acid Activated Siththandy Clay, RKC- Raw Kommadurai Clay AAKC- Acid Activated Kommadurai Clay). Note: RSC curve is overlapped on AASC curve.

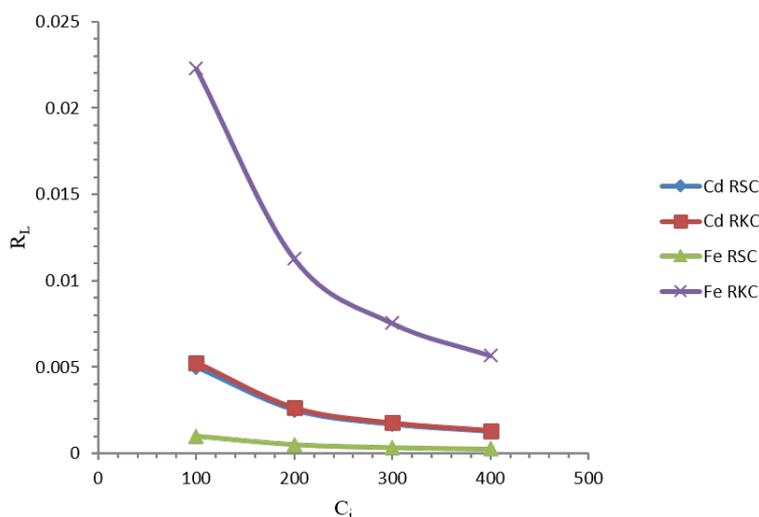


Figure 8: Effect of initial metal ion (Cd(II) ions and Fe(III) ions) concentrations on the separation factor, R_L : Cd RSC-Cadmium adsorption by raw Siththandy clay, Cd RKC -Cadmium adsorption by raw Kommathurai clay, Fe RSC-Iron adsorption by raw Siththandy clay and Fe RKC - Iron adsorption by raw Kommathurai clay. Note: Cd RSC curve is overlapped on Cd RKC.

Freundlich isotherm

The Freundlich adsorption isotherm study was performed and Freundlich constants which correspond to adsorption capacity (K_f) and the adsorption intensity (n) were obtained from the slope and intercept of the linear plot of $\ln q_e$ versus C_e and the results are given in Table 3 and Table 4. The results show that the favorability of these adsorption processes could be identified from the value of n . In this study, the value of n is greater than 1 in most of the cases indicating that the adsorption process is favorable.

The comparison of the values of correlation coefficient (R^2) in the above Tables 1 - 4 indicate that Langmuir adsorption isotherm gives a better fit than the Freundlich model for CR, Fe(III), and Cd(II) ions adsorption by these two types of raw clay minerals. This shows that the adsorption process occurs at particular homogeneous sites on the surface of the clay. The correlation coefficients, R^2 , for the fitting of CR adsorption data from both types of

acid-activated clays to Freundlich and Langmuir adsorption isotherms are compared and shows that the Freundlich adsorption isotherm gives a better fit for CR than the Langmuir adsorption. This indicates that the adsorption processes occur on heterogenous sites on the surface of the acid-activated clay.

These raw clay minerals show good adsorption efficiency over the Cd(II) and Fe(III) ions and this adsorption efficiency are similar to the works reported previously by researchers (Bhattacharyya *et al.*, 2006; Galindo *et al.*, 2013; Ayub *et al.*, 2020; Khalfa *et al.*, 2021). Moreover, the adsorption efficiency of the local clay over CR is improved by their acid activation and this is similar to the research published in the literature (Taher *et al.*, 2019; Silva *et al.*, 2021). Furthermore, these clay minerals are abundantly available in these areas and therefore, these low-cost clays are good candidates for the removal of CR, Cd(II), and Fe(III) ions from the aqueous medium.

Table 3: Freundlich adsorption isotherm constant for CR.

Adsorbent	K_f	n	R^2
Raw Siththandy Clay	0.2830	1.02	0.84
Acid Activated Siththandy Clay	0.000227	3.94	0.89
Raw Kommathurai Clay	1.678	1.53	0.80
Acid Activated Kommathurai Clay	520.1	0.91	0.74

Table 4: Freundlich adsorption isotherm constant for Cd(II) and Fe(III) ions.

Adsorbent	K_f		n		R^2	
	Cd(II)	Fe(III)	Cd(II)	Fe(III)	Cd(II)	Fe(III)
Raw Siththandy Clay	1.156	1.663	1.04	1.41	0.92	0.89
Raw Kommathurai Clay	2.388	4.810	1.40	1.07	0.87	0.85

CONCLUSION

In this work, two locally available clay minerals, Siththandy clay, and Kommathurai clay were used to study their adsorption efficiency against heavy metals such as Cd(II) ions and Fe(III) ions and the Congo red dye (CR) from wastewater. The adsorption efficiencies of these clays increased with contact time and initial concentration of the adsorbates. The maximum adsorption efficiencies for these adsorbates were obtained at the contact time of 24 h with the initial concentration of 400 mg L⁻¹. The research outcome showed that the raw clays can be used to remove nearly 80% of CR from aqueous solutions, whereas the adsorption of this dye could be achieved more than 90% after the acid activation. Moreover, these raw clays were also a good candidate for the adsorption of cadmium and ferric ions from aqueous solutions, and more than 75% of Cd(II) and Fe(III) ions were removed by these raw clay minerals. Adsorption isotherm studies showed that the Langmuir adsorption isotherm gave a better fit for CR, Fe(III) ions, and Cd(II) ions adsorption by the two types of raw clays, whereas CR adsorption by acid-activated clays showed a better fit to Freundlich isotherm. This concludes that these two types of raw and acid-activated clays are effective and low-cost adsorbents for the removal of CR, Cd(II), and Fe(III) ions from the aqueous medium.

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DECLARATION OF CONFLICT OF INTEREST

The authors have no conflicts of interest regarding the publication of this paper.

REFERENCES

- Ali, I., Asim, M. and Khan, T.A. (2012). Low-cost adsorbents for the removal of organic pollutants from wastewater. *Journal of Environmental Management* **30**: 170 - 183. DOI: <https://doi.org/10.1016/j.jenvman.2012.08.028>.
- Allègre, C., Moulin, P., Maisseu, M. and Charbit, F. (2006). Treatment and reuse of reactive dyeing effluents. *Journal of Membrane Science* **269**: 15 - 34. DOI: <https://doi.org/10.1016/j.memsci.2005.06.014>.
- Ayub, N., Ehsan, A.M. and Chaudhry, M.N. (2020). Using acid-activated azad Kkashmir clays to remove Cadmium and Lead ions from wastewater. *Polish Journal of Environmental Studies* **29**: 3041 - 3047. DOI: <https://doi.org/10.15244/pjoes/114501>.
- Bhattacharyya, K.G. and Gupta, S.S. (2006). Adsorption of Fe(III) from water by natural and acid activated clays: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions. *Adsorption* **12**: 185 - 204. DOI: <https://doi.org/10.1007/s10450-006-0145-0>.
- Borchardt, G. (1977). *Montmorillonite and Other Smectite Minerals*. Soil Science Society of America Madison, Wisconsin, 293 - 330.
- Fil, B.A., Özmetin, C. and Korkmaz, M. (2014). Characterization and electrokinetic properties of montmorillonite. *Bulgarian Chemical Communications* **46**: 258-263. DOI: <https://hdl.handle.net/20.500.12462/8495>.
- Friberg, L., Elinder, C.G. and Kjellstrom, T. (1992). *Cadmium, Environmental Health Criteria*. World Health Organization, Geneva, Switzerland.
- Galindo, L.S.G., Neto, A.F.D., Silva, M.G.C.D. and Vieira M.G.A. (2013). Removal of Cadmium(II) and Lead(II) ions from aqueous phase on Sodic Bentonite. *Materials Research* **16**: 515 - 527. DOI: <https://doi.org/10.1590/S1516-14392013005000007>.

- Han, H., Rafiq, M.K., Zhou, T., Xu, R., Mašek, O. and Li, X. (2019). A critical review of clay-based composites with enhanced adsorption performance for metal and organic pollutants. *Journal of Hazardous Materials* **369**: 780-796. DOI: <https://doi.org/10.1016/j.jhazmat.2019.02.003>.
- Karnib, M., Kabbani, A., Holail, H. and Olama, Z. (2014). Heavy metals removal using activated carbon, silica and silica activated carbon composite. *Energy Procedia* **50**: 113 - 120. DOI: <https://doi.org/10.1016/j.egypro.2014.06.014>.
- Kausar, A., Iqbal, M., Javed, A., Aftab, K., Nazli, Z-i-H., Bhatti, H.N. and Nouren, S. (2018). Dyes adsorption using clay and modified clay: A review. *Journal of Molecular Liquids* **256**: 395 - 407. DOI: <https://doi.org/10.1016/j.molliq.2018.02.034>.
- Khalifa, L., Cervera, M.L., Souissi-Najjar, S. and Bagane, M. (2021). Removal of Fe(III) from synthetic wastewater into raw and modified clay: Experiments and models fitting. *Separation Science and Technology* **56**: 708 - 718. DOI: <https://doi.org/10.1080/01496395.2017.1323923>.
- Komatsu, K., Urano, Y., Kojima, H. and Nagano, T. (2007). Development of an iminocoumarin based zinc sensor suitable for ratiometric fluorescence imaging of neuronal zinc. *Journal of American Chemical Society* **129**: 13447e54. DOI: <https://doi.org/10.1021/ja072432g>.
- Laws, E.A. (2018). *Aquatic Pollution: An introductory Text*. Wiley Publications, Los Angeles, US.
- Momina, Shahadat, M. and Isamil, S. (2018). Regeneration performance of clay-based adsorbents for the removal of industrial dyes: a review. *RSC Advances* **8**: 24571 - 24587. DOI: <https://doi.org/10.1039/C8RA04290J>.
- Nir, T.P.S., Zadaka, D., Rabinovitz, O., Serban, C., Groisman, L. and Rubin, B. (2005). Water purification from organic pollutants by optimized micelle-clay systems. *Environmental Science and Technology* **39**: 2343 - 2348. DOI: <https://doi.org/10.1021/es049251o>.
- Oubagaranadin, J.U.K. and Murthy, Z.V.P. (2010). Characterization and use of acid-activated montmorillonite-illite type of clay for Lead(II) removal. *American Institute of Chemical Engineers* **56**: 2312 - 2322. DOI: <https://doi.org/10.1002/aic.12164>.
- Parker, J.C., Amos, D.F. and Zelazny, L.W. (1982). Water Adsorption and swelling of clay minerals in soil systems. *Soil science society of American Journal System* **46**: 450 - 456. DOI: <https://doi.org/10.2136/sssaj1982.03615995004600030002x>.
- Ricart, M.T., Pazos, M., Gouveia, S., Cameselle, C. and Sanromán, M.A. (2008). Electrokinetic removal of organic pollutants removal of organic pollutants and heavy metals in soils by electrokinetic remediation. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering* **43**: 871 - 875. DOI: <https://doi.org/10.1080/10934520801974376>.
- Satarug, S., Baker, J.R., Urbenjapol, S., Haswell-Elkins, M., Reilly, P.E., Williams, M.R. and Moore, D.J. (2003). A global perspective on cadmium pollution and toxicity in nonoccupationally exposed population. *Toxicology Letters* **137**: 65e83. DOI: [https://doi.org/10.1016/s0378-4274\(02\)00381-8](https://doi.org/10.1016/s0378-4274(02)00381-8).
- Schweitzer, L. and Noblet, J. (2018). Chapter 3.6 - Water contamination and pollution. In: *Green Chemistry: An Inclusive Approach* 261 - 290.
- Sennour R., Mimane G., Benghalem A., Taleb S. (2009). Removal of the persistent pollutant chlorobenzene by adsorption onto activated montmorillonite. *Applied Clay Science* **43**: 503 - 506. DOI: <https://doi.org/10.1016/j.clay.2008.06.019>.
- Siddique, H.M.A. and Kiani, A.K. (2020). Industrial pollution and human health: evidence from middle-income countries. *Environmental Science and Pollution Research* **27**: 12439-12448. DOI: <https://doi.org/10.1007/s11356-020-07657-z>.
- Silva, V.C., Araújo, M.E.B., Rodrigues, A.M., Cartaxo, J.M., Menezes, R.R. and Neves, G.A. (2021). Adsorption behavior of acid-treated brazilian palygorskite for cationic and anionic dyes removal from the water. *Sustainability* **13**: 3954 - 3976. DOI: <https://doi.org/10.3390/su13073954>.
- Srinivasan, R. (2011). Advances in application of natural clay and its composites in removal of biological, organic, and inorganic contaminants from drinking water. *Advances in Materials Science and Engineering* 2011. DOI: <https://doi.org/10.1155/2011/872531>.
- Taher, T., Rohendi, D., Mohadi, R. and Lesbani A. (2019). Congo red dye removal from aqueous solution by acid-activated bentonite from sarolangun: kinetic, equilibrium, and thermodynamic studies. *Arab Journal of Basic and Applied Sciences* **26**: 125 - 136. DOI: <https://doi.org/10.1080/25765299.2019.1576274>.
- Tan, I.A.W., Ahmad, A.L. and Hameed, B.H. (2009). Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2,4,6-trichlorophenol on oil palm empty fruit bunch-based activated carbon. *Journal of Hazardous Materials* **164**: 473 - 482. DOI: <https://doi.org/10.1016/j.jhazmat.2008.08.025>.
- Toor, M.K. (2018). Enhancing Adsorption Capacity of Bentonite for Dye Removal: Physicochemical Modification and Characterization. *MATEC Web of Conferences* **144**: 02021. DOI: <https://doi.org/10.1051/mateconf/201814402021>.
- Uddin, M.K. (2017). A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. *Chemical Engineering Journal* **308**: 438 - 462. <https://doi.org/10.1016/j.cej.2016.09.029>.
- Vimonses, V. (2011). Development of Multifunctional Nanomaterials and Adsorption-Photocatalysis Hybrid System for Wastewater Reclamation Doctoral Thesis, University of Adelaide.