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ENVIRONMENTAL AND HYDRAULIC MONITORING USING CATIONIC DYES TO INVESTIGATE THE BARRIERS EFFECT ON KAOLIN DEPOSITION

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Abstract: Dyes are used in hydraulic fields such as hydraulic tracking to show the flow path, monitor flow lines within a ground dam, or track the spread of contaminated water within horizontal pipes and environmental fields as environmental indicators in titrations, such as titration of precipitate composition. Some environmental experiments dispense with the dye's use because it interferes with other compounds, such as interfering with the turbidity readings even if non-reactive dyes, but the present study transformed this problem into a positive phenomenon to benefits from the dye in both fields. The research methodology includes a laboratory analysis using different parameters such as discharge of suspension, the volume of dye, and the percentage of initial water depth at maximum water depth also theoretical analysis of the previous research methodology. The experimental results show that cationic dyes' absorption (methylene blue dye, MB and crystal violet, CV) is directly proportional to the percentage of kaolin deposition in the sedimentation tank areas. Finally, MB and CV dyes are used in both fields in one trial(such as tracking flow movement, monitoring the vortices formed using baffles, and inter between the amount of kaolin precipitated in each zone the sedimentation). However, MB is the best compare to CV.

Keywords: *absorbance of the dye, hydraulic fields environmental fields, kaolin deposition, sedimentation tank area, cationic dyes, baffles*

1. Introduction

China discovered the original reference of kauling mine. Kaolins are generally classified as primary or secondary deposits. Primary Kaolins are formed by alterations of crystalline rocks such as granite and are found in the location where they were created. Secondary kaolin deposits are sedimentary and are formed by the erosion of primary deposits .As the eroded materials are washed downstream, separation takes place by gravity and particle size. The finer and lighter kaolin particles are carried farther and eventually deposit in lakes, estuaries, and lagoons where secondary deposits may be formed and Blake [1].

Kaolins are suspensions that possess clotting behaviours of low electrolyte concentrations (lower zeta-potential for suspension stability), allowing a broad pH range for suspension stability. These zeta-potentials are negative over a broad pH range,48-50, and the zeta-potential presumably lies between alumina and silica[2-3]. Kaolinite particle suspended in a liquid dictate the magnitude of the van der Waals attractive forces between the particles ($expressed\ by\ A_{eff}$) is almost an order of magnitude larger than silica and a factor of 7 lower than that of alumina. Therefore, kaolinite

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particles inherently are easier to disperse than alumina[4].

Dyes can be classified into three types according to their nuclear structures: anionic dyes (acidic and reactive), nonionic dyes (disperse), and cationic dyes (basic) [5]. Organic cationic dyes like methylene blue(MB) and crystal violet (CV) are considered more toxic than anionic ones [6]. In general, those dyes adsorb on clay in amounts higher than the cation exchange capacity (CEC maximum number of cations adsorbed on the clay).

Methylene dye is also called methylthioninium chloride with the chemical formula (C16H18CIN3S) with a molecular weight (319.85 g / mol). The maximum light absorption is near 670 nanometers[7]. The absorption properties depend on several factors, including protons and the absorption of other materials. Methylene dye is used to identify some ions in water, such as carboxylate ions, phosphates, sulphates, and sulfones. It can be used to determine the amount of fine aggregate, as the amount of methylene blue reflects the amount of clay minerals in the collected samples. A blue methylene solution is added to the fine aggregate that is stirred with water[8].

Several studies have investigated the effect of clay-dye interactions on dye removal; for example, Researchers[9] separate crystal violet and methylene blue dyes from water by surface-functionalized zirconium silicate nanocomposite. They were examined pH for aqueous solutions to choose the optimal state for pH of each dye, the effect of the reaction time of dyes with the substance used on the removal, impact of the doses of the substance, the effect of the dye concentrations on the removal and impact of the introduction of different salts such as NaCl, KCL etcetera.

Researchers [10] studied MB, CV, and CR adsorption on clays to assess the behaviour of these three dyes in the two- and triple mixtures and to study the effect of percentage, contact time, initial dye concentration, temperature, and pH of the initial dye solution on adsorption. Isorption isotherm, kinetic models, and thermodynamic studies to describe the mechanism involved in the adsorption process.

Researchers [11] investigated local soil use to remove MB and CV dyes from the binary system. Also studied the kinetics of different aspects affecting the adsorption procedures such as dye concentration, soil dose, pH, and temperature.

Researchers in[12] presented a review for a comprehensive explanation of the absorption of the various chemical pollutants in an aqueous solution on a surface of Montmorillonite. The review clarified all the mechanisms related to the adsorption processes on it.

Cationic contaminants such as heavy metal cations and cationic dyes absorb on original Mt through the cation exchange. Still, heavy metal cations absorb on (AMt and TMt) through the cation exchange process. Both cationic and anionic contaminants absorb IMt through ion exchange or absorption or surface precipitation or structural inclusion.

OMt has completely different properties in the microstructure and absorption, depending on the used organic modifiers. Absorption of anionic pollutants occurs by anion exchange, but heavy metal cations absorption occurs through specific reactions. Synergistic absorption of inorganic cations and anions were observed on IMt by forming triple complexes and surface sedimentation, IOMt as multi-functional adsorbents can absorb HOC by partitioning/desorption and anionic pollutants through anion/bonding exchange. They can also remove HOC through a combined process between adsorption and degradation.

In this paper, two cationic dyes, CV and MB, use it as an environmental guide for comparison between the percentage of kaolin removed in each area within the sedimentation tank, which was shown through personal vision (visual follow-up of the experiment)and monitoring the gradation of dyes in each area. Also, by performing absorption, turbidity, and pH tests.

2. Experimental work

2.1.Pilot design Setup, Equipment, Operation

- *Sedimentation model*

The sedimentation process is observed in a laboratory model of a sediment formation tank obtained from Armfield Engineering (UK). The tank is 100 cm in length, 40 cm in width, 25 cm in-depth, and 20 cm in depth. The slope of the tank bottom was zero. Three partitions are placed in the basin at distances from the entrance of 20 cm, 50 cm, and 80 cm, respectively. The two bulkheads' height from the bottom (the opening or opening of the gate) was 0 cm, 3 cm, and 6 cm, as shown in "Fig. 1". With a maximum capacity of 120 liters, the feeding tank was used to mix fresh water with kaolin continuously using a circulation pump. Fixation of suspension flowrate (after calibration rate by volumetric transfer method) at 1 L / min via gate valve and flow meter.

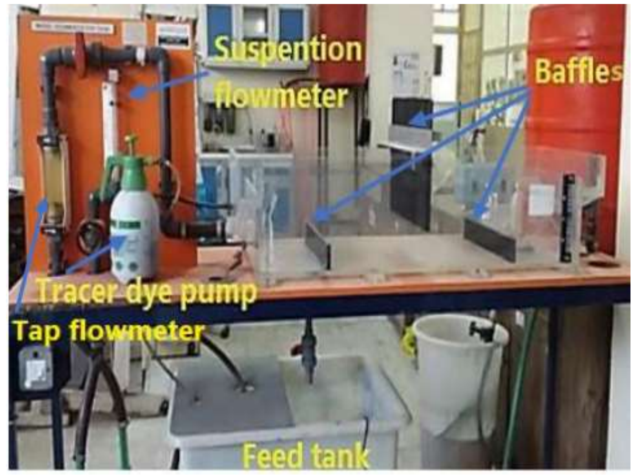

Figure 1. Laboratory sedimentation tank model

Table1. Suspension flowmeter calibration

Inlet discharge(m^3/s)	Outletdischarge(m^3/s)
1	1.8
1	1.19
1	1.18
1	≅ 1.01

Table 2. Tap flowmeter calibration

Inlet discharge(m^3/s)	Outlet discharge(m^3/s)
4	3.27
4	3.4
5	5.5
5	≅ 5.08

- *Turbidimeter*

The test sample is entered into a turbidimeter, as shown in "Fig.2", and the cap is closed, then the red button is pressed to record the reading for calibration. The bottle is filled with the sample until the filling line and places back cover again after removing the fingerprints by wiping outside the sample container. Then, the sample bottle is inserted into the turbidity meter, close the cap, and take a reading by pressing the red button to record the turbidity value in the Nephelometric Turbidity Unit (NTU).

Figure2. Hatch 2100Q turbidity meter

- *pH-meter*

Thermo Orion 4-star pH ISE Benchtop meter, as shown in "Fig.3", used to measure the suspended solution's pH and temperature after adding the dyes to it. The device is calibrated before using it with a known pH buffer solution. The device's electrode bracket is washed with distilled water and dried well, after which 10 ml of suspension is taken with the dye in each area inside the sedimentation basin and added in a small baker. The device's electrode is placed inside the small baker and moving it until the reading is confirmed on the device.

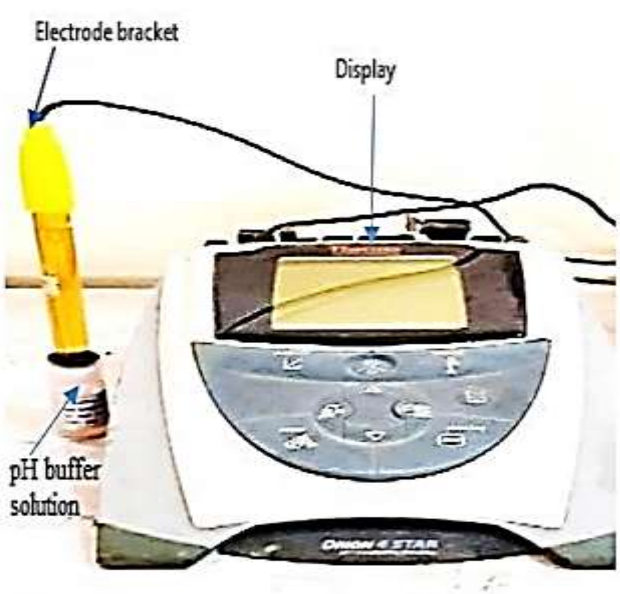

Figure 3. Thermo Orion 4-star pH ISE Benchtop meter

- *Spectrophotometer*

The absorption spectrophotometer is an instrument used to measure absorbed light intensity as a wavelength function, as shown in "Fig.4".

A spectrophotometer warms up for 45 minutes, then the select wavelength of dyes (CV, MB) to calibrate before using the device for an empirical sample as shown in "Fig.5" and "Fig.6".The sample was prepared in a 1cm square glass call and place in a spectrophotometer, then close the device's lid to record the reading in the display.

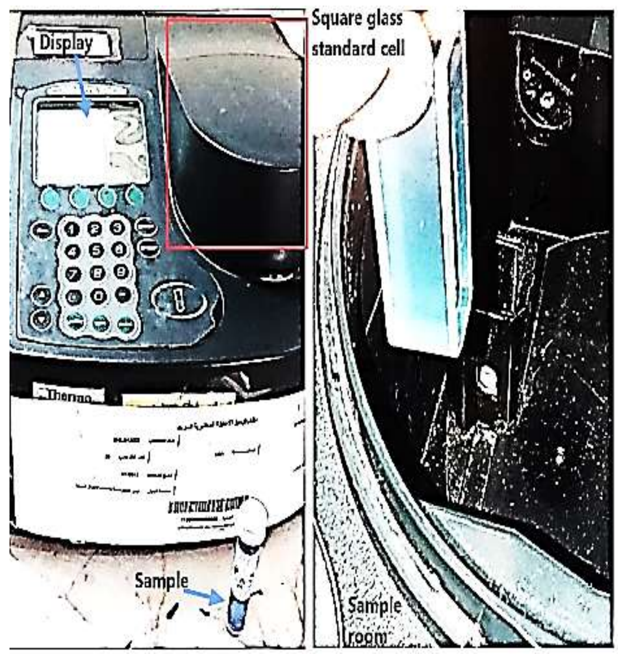

Figure4. Spectrophotometer made in the USA

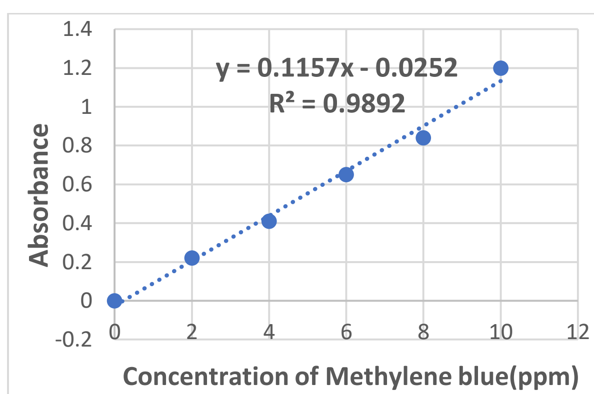

Figure 5. Calibration curve for MB in ppm

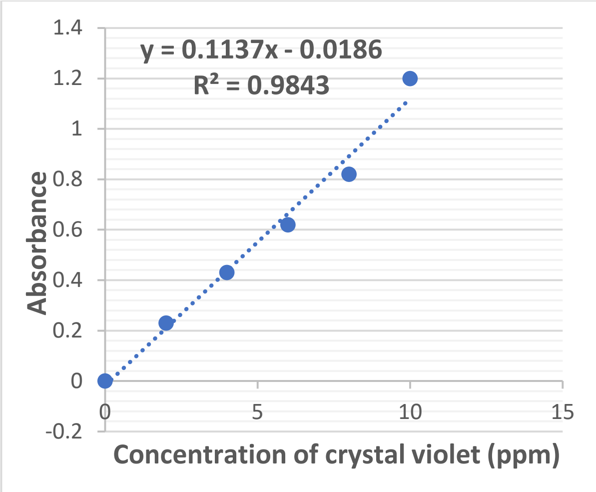

Figure 6. Calibration curve for CV in ppm

2.2. Experimental Operating Conditions and Their Limitations

Operation condition

The experiments are conducted in the October season inside the water treatment laboratory at the Department of Environment Engineering/Al-Mustansiriya university at constant temperature(25℃) and atmospheric pressure.

Operation limitations

- The design changes made for the study on the sedimentation basin, which included linking tap flowmeter with suspension flowmeter using a Y-fitting cause problem. Accumulation of clays at the bottom of the feeding basin is clogged discharge pump caused backflow and explode draw pipe in the continuous discharge operation.

- The problem of cleaning the sedimentation basin with barriers requires removing barriers after each trial.

- Each experiment requires a very large time to prepare a fixed suspension concentration, requiring the inward concentration. The device is not equipped with a dosing pump, followed by taking samples and measuring them constantly.

- The suspension flowrate needs to be constantly monitored because his reading is constantly dropping, affected by the entry water pump.

2.3. Preparation Suspension and Tracer Dye

Preparation of suspension or slurry that its turbidity within the range of 50 NTU by adding different industrial kaolin quantities until obtaining the turbidity required. It achieved in this experiment by adding 21.9g of kaolin inside 119L feed tank(tank supply sedimentation basin filled with tap water(10 NTU, turbidity measured using of turbidity meter device).

The amount of kaolin to be added was determined inside 119 L to prepare 50NTU after making the table below prepared from the experiment data to add different quantities shown in the tables inside a baker filled with 1 liter of water with 10NTU to know the degree of kaolin stability shown in "Fig. 7".

Table 3. Different turbidity of different percentages of kaolin over time

Kaolin weight(g)	Turbidity(after 0 min)	Turbidity (after 10min)
0.0106	8.80	7.04
0.05	40.25	29.77
0.1	55.68	36.37
0.25	142.4	88.56
1	773	152.8
5	870.1	258.9
10	402.6	285.1

Figure 7. Mixing kaolin using a Hotplate Stirrer

The dyes(MB and CV) added in this experiment do not change the water density. 3gm packet of dye (MB or CV) is used and pour the contents along with 1 liter of deionized or distilled water into the 1-liter bottle (supplied) then is Shaked mixture before it inters to the basin.

3. Sampling Take and Absorption Measured

The samples are collected for examination of physical and chemical properties by plastic tubes (10 ml). Samples are taken raw water, water settled in each zone inside the basin, and treated water. The physical and chemical properties of samples are conducted by the equipment available in the Water treatment lab, located inside the Environmental Department in the College of Engineering in Al-Mustansiriya University/Iraq.

When kaolin precipitates inside the basin, and before adding the dye(MB or CV), Samples are taken to measure the turbidity. At the same experiment, under the same conditions, the dye(MB or CV) is added. Samples are taken from the same areas in which it was taken before adding dye. The dye absorption (MB or CV) is measured using a spectrophotometer, extracting the pH and temperature.

4. Result and Dissection

"Fig.8" shows a correlation of percentage removal of the two dyes with the amount of kaolin deposited at the bottom of each zone of the sedimentation tank.

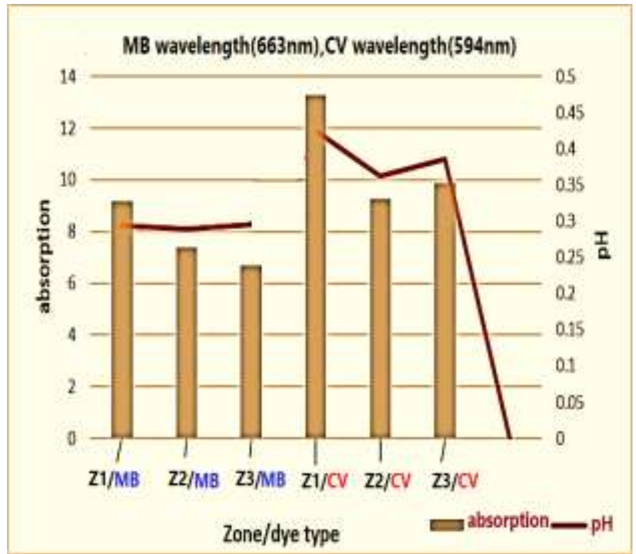

Figure 8. Relationship between pH and absorption and its change with two cationic(basic) dyes inside three zones of the sedimentation tank at temperature 25 ℃

Given that both MB and CV are basic dyes, it is noticed that pH is higher than 7, but it is clear that CV base dye is stronger; for this reason, the solution's tendency is more basic. Also, the dye's absorbance with a strong base is higher. The adsorbent meaning is less, and vice versa for its dye MB, which corresponds to the study performed by Omer et al. (2018), which states about removing both dyes using palm kernel fiber.

Higher wavelengths of basic dyes have higher absorption and pH higher, so their absorption on the kaolin deposited surface is lower.

Table 4. Changing absorbance of the dye within the sedimentation basin areas by changing turbidity, change the volume of the dye, change discharge of inlet suspension, and percentage of initial depth water at the optimum depth of water.

zone	Initial depth water /optimum depth	Turbidity , NTU	Absorption at add 5ml of CV	Absorption at add 10 ml 0f CV
Q=1L/min , inlet turbidity =50 NTU, add crystal violet (CV, Concentration 3g/l, wavelength=594nm)				
1	0.15	16.7	0.063	0.63
2		14.3	0.216	2.16
3		12.6	0.275	2.75
1	0.3	9.56	0.055	0.55
2		8.85	0.282	2.82
3		9	0.232	2.32
Q=5L/min , inlet turbidity =50 NTU, add 10 ml 0f crystal violet (CV, Concentration 3g/l, wavelength=594nm)				
1	0.3	23	0.051	0.102
2		21.8	0.142	0.284
3		22.1	0.202	0.403

"Table 4" shows that the absorbance of the dye inside the sedimentation tank areas on the surface of the deposited kaolin changes when changing the volume of the added dye; as the more dose is reduced, the absorbance decreases. It decreases because the sedimentation tank deposits settle in the form of layers whose concentration starts from the bottom, as shown in "Fig.9" and "Fig.10" . The contact time between the dye and the kaolin increased. As for the change of discharge, it affects the turbidity. Thus, the absorbance is affected.

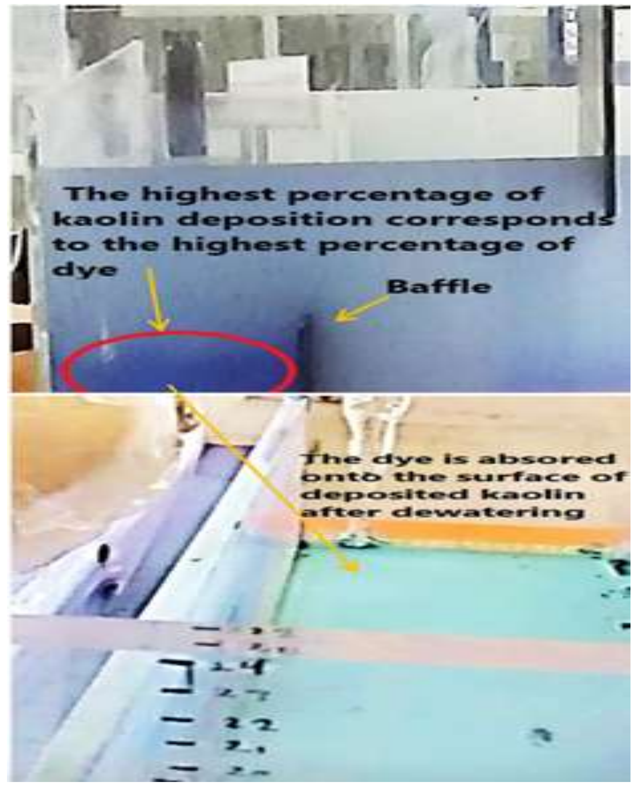

Figure 9. Deposition of MB dye on the surface of kaolin before and after dewatering

“Fig.9 "indicates that the dye concentration is at the bottom of the sedimentation basin before dewatering, and after dewatering, dye removal on the surface of the kaolin precipitated. The quantity of clays deposited at the bottom; is consistent with MB's water testing role in Gomaa et al.,(2019).

The removal due to physical adsorption because kaolins are colloidal substances containing a negative electrical charge increases as the pH increases mentioned by Guo, Yuan, and (Bill) Yu, Xiong(2017), and Kai He et al. (2019). The attraction between kaolin and cationic dyes is why the dyes are adsorbed on the kaolin surface.

Kaolin removes the two dyes on its surface because kaolin contributes to mesporous silica formation (Shu, Z, et al., 2016), and mesoporous silica enhanced MB and CV uptake, as mentioned (Liang, Z, et al., 2016).

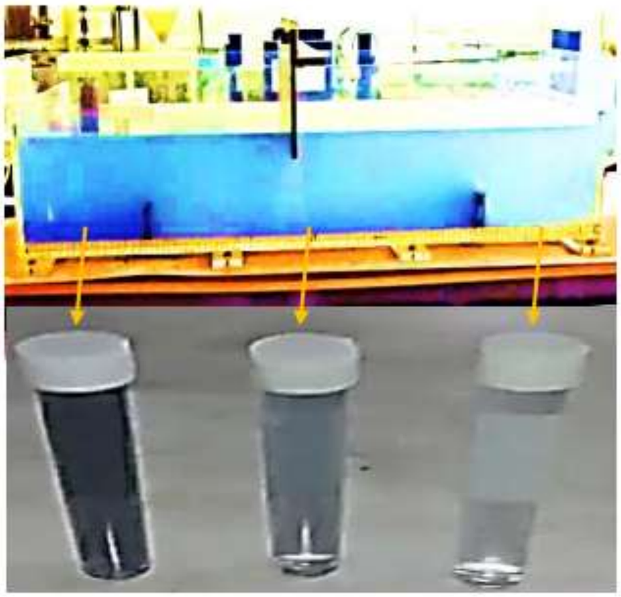

Figure10. Dye graduated through the sedimentation tank areas

All above indicates that the dye can be used in environmental fields to guide the largest removal of kaolin inside sedimentation tank areas, a quotation from the principle of using dye as an indicator to titration sediment formation.

"Fig .11"is an illustration of the use of the dye in hydraulic fields

Figure11. A dye is used in hydraulic fields as a hydraulic tracer to monitoring short-circuit and the impact of the baffle on flow inside the sedimentation tank

4. Summary

At the beginning of the experiment, the kaolin was deposited inside a sedimentation basin equipped with barriers and then taking the turbidity readings in each area. The dye was used for hydraulic tracking of the flow paths and vortices formed by barriers. Still, once the dye entered and distributed within the places of a sedimentation basin, it founded that the spread of dye increased in places of increase of the turbidity (confirmed by measure the absorbance of each sample). After the water's disposal inside the sedimentation basin, it was noticed that the dye was removed on the surface of kaolin deposited at the bottom at high pH and normal temperature (environmental monitoring of the highest removal rate). Many types of research related to removing dyes on the kaolin surface were studied that show increase pH reduces the zeta potential on the kaolin surface; therefore, the adsorption of dyes on the active sites with kaolin increases.

6. Conclusions

1- Both cationic dyes (MB and CV) can guide the environmental removal of kaolin slurry inside sedimentation tank areas at different inlet parameter such as discharge of suspension, a volume of dye, and the initial height of water at maximum
2- The removal took place due to physical or polar adsorption. It is expected that there will be no or less ionic exchange because these dyes have more adsorption than their ionic exchange capacity with this.
3- Adsorption of MB dye on kaolin deposited on the bottom of the sedimentation basin is higher than that of its CV.

4- 4-In the future, tests of samples from this formed layer are required to know their chemical composition. It is also possible to test other dyes or other deposits.

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Conflict of interest

The authors declare no conflict of interest in publication of this research.

Abbreviations

A list of symbols should be inserted before the references if such a list is needed

MB	Methylene blue dye
CV	Crystal violet dye
CBC	Cation exchange capacity
Mt	Montmorillonite
AMt	Acid-washed montmorillonite
TMt	Thermal-treated montmorillonite
OMt	Organo-montmorillonite
HOC	Hydrophobic organic contaminants
IMt	Inorganic modifiers modified Montmorillonite
IOMt	Inorganic and organic modifiers modified montmorillonite
NTU	Nephelometric Turbidity Unit

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