Journal of Basic Physical Research ISSN: 2141-8403 Prints, 2141-8411 Online
Vol.11, No.1 pp. 10- 22, March., 2023. Available online at www.jbasicphyres-unizik.org

REMOVAL OF SOME ORGANIC POLLUTANTS FROM AQUEOUS ENVIRONMENT USING PEROVSKITE NANOPARTICLES

Onwukeme, V.I. and Ikezuagu, B.C.
Department of Pure And Industrial Chemistry, Nnamdi Azikiwe University, Awka.
Corresponding Author's Mail: cb.ikezuagu@unizik.edu.ng

Abstract
The toxic effects of some organic pollutants on human and the aquatic life are of serious concern. The need for removal of these pollutants from aqueous environment led to the use of adsorption techniques as a cheap and efficient treatment method. In this research, mixed metal oxide (Perovskite) was synthesised through coprecipitation method. It was characterised by FTIR and XRD analysis, further characterisation was done for bulk density, particle density, pore volume, % pore space, % solid space and surface area. Batch adsorption was conducted using the synthesised adsorbent for the removal of tartrazine, BHT and dioxane from aqueous environment. Various parameters such as contact time, adsorbent dosage, initial concentration, pH and temperature were studied to observe their effect in the adsorption process. FTIR spectra showed eleven absorptions at 693.28484 cm^{-1}, 838.65101 cm^{-1}, 1021.29057 cm^{-1}, 1148.02005 cm^{-1}, 1401.47903 cm^{-1}, 1561.75455 cm^{-1}, 1871.12359 cm^{-1}, 2109.67322 cm^{-1}, 2366.85953 cm^{-1}, 3186.87385 cm^{-1}, 3548.42562 cm^{-1} indicating the presence of aromatic derivatives, halo compound, vinyl ether, aliphatic ether, sulfone, nitro compound, anhydride, isothiocyanate, carbondioxide, carboxylic acid and alcohol respectively. XRD spectra showed no peak revealing that the synthesized perovskite is not a crystal. The experimental equilibrium adsorption data fitted better to the freundlich isotherm model than the Langmuir isotherm model. The kinetic data conformed better to pseudo second order model than the pseudo-first order model. The adsorption of tartrazine, BHT and dioxane were non spontaneous for all the adsorption at the temperatures under investigation. The result of this study shows that this mixed metal oxide can be used as effective adsorbent for the removal of contaminants from aqueous environment.
Keywords: *Pollutants, Adsorption, Kinetics, Thermodynamics, Perovskite, Nanoparticles*

Introduction

In Nigeria, the level of pollution of environment is so alarming. There is still indiscriminate disposal of waste in gutters, road sides and streets. These pollutants end up in our water bodies polluting them. No legislation or enforcement regarding the control of these pollutants is effective. Perovskites are a class of mixed oxides, which have interesting catalytic and physicochemical properties. A novel method developed for the synthesis of perovskites of the type $LaMO_3$ (M = Mn, Fe, Co, Cr, Al) involves microwave irradiation for just 15 min using oxalate precursors. The $LaMO_3$ perovskites were used as catalysts for reduction of aromatic nitro compounds with propan-2-ol as hydrogen donor and KOH as promoter. Notably, $LaFeO_3$ perovskite is the best catalyst under the same reaction conditions. The corresponding aniline derivatives are obtained in excellent yield (78–98%) in 2 to 6 hours. The method is simple and does not involve intermittent grindings and calcinations at elevated temperatures, effective for many organic reactions as environment-friendly acid–base catalysts (Heinz et al., 2000; Watanabe & Koyasu, 2000). However, the most common use for mixed metal oxides (MMOs) has been in the area of catalysis and they have found use both as the catalyst and as catalyst supports (Heinz et al., 2000; Watanabe & Koyasu, 2000). Specifically, MMO containing aluminum has found many opportunities in catalysis (Corma, 1995; Reddy & Subrahmanyam, 1992; Kiessling et al., 1991).

The introduction of the contaminant to water sources is attributed to dioxane being a byproduct to many domestic commercial products, improper disposal of industrial waste, and past solvent spills not completely remediated. Due to dioxane's complete miscibility with water, most organic solvents, aromatic hydrocarbons, and oils, volatilization and sorption prove to be inconsequential mitigation mechanisms for contaminated sources (Zenker et al., 2003).BHT is a common antioxidant and has been implicated in oil foods and food packaging materials as a

substance that could migrate into the food supply chain and cause suppression of human respiratory enzymes (Yehye et al., 2015). A significant problem arises also from the fact that azo dyes are polluted with aromatic amines during the manufacturing process (Yehye et al., 2015). The most frequent pollutant of tartrazine is benzidine. The synthesis of tartrazine uses sulfanilic acid which in turn is prepared from aniline. Benzidine is the only possible product of aniline oxidation and is often detected as a residue. It also forms benzidine dye derivatives being health hazard pollutants (Burton & Ingold, 1981). Water pollution can be defined as any adverse change in conditions or composition of water so that it becomes less suitable or unsuitable for the purpose for which it would be suitable in its natural state (Yogesh, 2012).

Mixed metal oxides nanoparticles have large surface area and great versability in binding specific functional group for specific contaminants which make them ideal candidates for the design and development of innovative adsorption strategies. Mixed metal oxides nanoparticles can perform some functions as catalyst for oxidative degradation of the pollutants and at some time minimize secondary contamination events. To this, highly oxidising species are activated in the presence of pollutants. So since removal, reuse and toxicity of catalyst are major concern, focus has been on use of heterogenous magnetic materials that can perform the functions (Pate et al., 2020). Chen et al. (2011) checked preparation and characterization of porous granular ceramic containing dispersed aluminium and iron oxide as adsorbents for fluoride removal from aqueous solution. Sajan et al., (2015) explored the applications of different mixed metal oxides for the capture of CO_2 and convert of CO_2 to syn-gas. Adsorption has been mostly used for the remediation of these pollutants (tartrazine, BHT and dioxane), but adsorbents like activated carbon which has been widely used for adsorption cannot be regenerated after adsorption. Since sorbent separation after adsorption is not easily achieved with the existing adsorbents, the use of mixed metal oxide nanoparticles for adsorption has been proven to make the task of sorption separation easy. The aim of this study is to remove tatrazine, BHT and dioxane from aqueous environment using synthesised mixed metal oxide nanoparticle.

Materials and methods

Synthesis of Perovskite, Characterisation and sorption

The Perovskite ($ZrCoO_3$) was synthesised by reacting 1:1 stoichiometric ratio of zirconium oxychloride (32.48 g of $ZrOCl_2$ in 50 ml of distilled water) and cobalt(II)chloride (23.89 g of $CoCl_2$ in 50 ml of distilled water), the two solutions were mixed properly in a 250 ml beaker and stirred for proper mixing, 10.01 g of starch dissolved in 50 ml of distilled water was added to the mixture and stirred, ammonium hydroxide was added drop wise to attain pH of 9 and the mixture was stirred for 2 hrs while heating, after heating it was cooled at room temperature, centrifuged, washed with distilled water and dried at 110^{o}C in an oven. Calcinations was done at 700^{o}C for 3 hrs then ground to a powder in a mortar. Physical properties of perovskite like bulk density, porosity, % pore space, % solid space and surface area were determined using standard methods (Weil and Brady, 2016 ; Menkiti et al., 2014 ; Monshi and Attar 2009)|. FTIR spectra were recorded in the region 4000-650 cm^{-1} on a Varian 600-IR series spectrometer using standard methods. X-ray diffraction analysis was made on the samples at room temperature using the PANalytical X'pert PRO X-ray diffractometer equipped with Cu-Ka radiation. The data collection was done with 2theta ranging from 0.0000 to 77.9647^o and the step width of 0.0260 with 29.0700 seconds per step counting time. The cell dimension for the crystal was determined using Bragg equation as follows:

Length of unit cell = $\lambda/2\sin\theta$ and cell volume was calculated from the multiples of the cell dimensions as follows:

Cell volume = a x b x c where a,b,c are cell dimensions, λ is wavelength and θ is angle of reflection.

Collection and preparation of solutions of adsorbates

The reagents used in this work were obtained from a commercial market without further purification. The stock solution of tartrazine was prepared by dissolving 100mg of the dye in 250ml of distilled water while the BHT stock solution was prepared by dissolving 100mg of BHT in 250ml of distilled water. The dioxane stock solution was prepared by dissolving 100mg of dioxane in 250ml of distilled water.

Adsorption studies

Effect of Contact Time on the Adsorption

The adsorbent mass of 1g was weighed into three distinct conical flasks. The concentration of 400mg/L of each of the adsorbates was prepared respectively using distilled water. 10ml of the solution was thereafter poured into the flasks. The three conical flasks were then tagged for the time interval of 20, 60 and 120 minutes as described by (Sumanjit et al., 2007). The flasks were then covered and agitated at the separate time interval. Towards the end of each time intervals, the suspensions were filtered and centrifuged. The concentration of the dye was measured with the aid of UV spectrophotometer (Sumanjit, et al., 2007).

Effect of Temperature on Adsorption

The adsorbent mass of 0.1g was weighed into three separate conical flasks and 400mg/L of each of the adsorbates was measured in each of the three flasks respectively. The flasks were labeled for temperature difference of 20^{o}C, 40^{o}C and 100^{o}C. The three flasks were then tightly covered and heated at their appropriate temperatures with the means of a thermostatic water bath at 20mins each. Towards the end of the experiment, each of the flasks were brought out and agitated for about 5 minutes. The accompanying suspensions were filtered and centrifuged. The dye ion concentration was measured using UV spectrophotometer. (Sumanjit, et al., 2007)

Effect of ion Concentration on Adsorption.

Solutions of 300,200 and 100 mg/L each of the adsorbates was prepared respectively, 10ml of each of the solution were added to 0.1 g of the adsorbent in the three separate conical flasks and then agitated for 20 minutes. The suspensions were filtered and centrifuged. The dye ion concentration was estimated using UV spectrophotometer.

Effect of pH on Adsorption

0.1 g of the adsorbent was weighed into three separate flasks, 10ml of concentration of 400 mg/L of each of the adsorbates was measured and added into each of the three flasks respectively. The solution was then adjusted to pH 2.0, 4.0, 6.0, 8.0 and 10.0 by adding a solution of HCl or NaOH and the pH reading were confirmed by the use of pH meter. The conical flasks were tightly covered and agitated for 20 minutes. The suspensions were filtered and centrifuged. The dye ion concentrations were measured via the UV spectrophotometer.

Effect of Adsorbent dosage on Adsorption

5.0 g, 3.0 g and 1.0 g of the adsorbent was weighed into three separate flasks, 10 ml of concentration of 400 mg/L of each of the adsorbates was measured in each the solution was measured and added into each of the three flasks respectively. The conical flasks were tightly covered and agitated for 20 minutes. The suspensions were filtered and centrifuged. The dye ion concentrations were measured via the UV spectrophotometer.

Results And Discussion

Table 2 Physical properties of the perovskite ($ZrCoO_3$)

Table 2 shows the physical properties of the perovskite ($ZrCoO_3$)

Property	**Perovskite**
Surface area(m^2g^{-1})	119
Bulk density (g/cm^3)	0.675
Particle density(g/cm^3)	1.220
Pore volume(cm^3)	0.447
% Pore space	44.7
% Solid space	55.3

The values of bulk density for all the adsorbents agree with the finding of Ariany et al. (2018) who reported that the bulk densities of activated carbon are usually between 0.3 – 0.7g/cm^3. Surface area is regarded as the most important property of adsorbents as the adsorption capacity of adsorbents is directly related to its surface area, a higher surface area allows a better adsorption. Perovskite has surface area of 119 m^2g^{-1} which fall within mesoporous materials, it also has potential application in heterogenous catalysis as catalyst or catalyst support. The pore volume is the indication of the porosity of the prepared material and directly related to the percentage pore space and solid space.

Table 3 Functional groups on the surface of the synthesised perovskite

	Functional groups	**Frequencies (cm^{-1})**	**Bonds**
Perovskite	Aromatic	693.28484	C-H bending
	Halo compound	838.65101	C-Cl stretching
	Vinyl ether	1021.29057	C-O stretching
	Aliphatic ether	1148.02005	C-O stretching
	Sulfone	1401.47903	S=O stretching
	Nitro compound	1561.75455	N-O stretching
	Anhydride	1871.12359	C=O stretching
	Isothiocyanate	2109.67322	N=C=S stretching
	Carbondioxide	2366.85953	O=C=O stretching
	Alcohol	3548.42562	O-H stretching

The FTIR spectra of perovskite shows eleven absorptions at 693.28484 cm^{-1}, 838.65101 cm^{-1}, 1021.29057 cm^{-1}, 1148.02005 cm^{-1}, 1401.47903 cm^{-1}, 1561.75455 cm^{-1}, 1871.12359 cm^{-1}, 2109.67322 cm^{-1}, 2366.85953 cm^{-1}, 3186.87385 cm^{-1}, 3548.42562 cm^{-1} indicating the presence of aromatic compound, halo compound, vinyl ether, aliphatic ether, sulfone, nitro compound, anhydride, isothiocyanate, carbondioxide, carboxylic acid and alcohol respectively.

Table 4 XRD Analyses Results of the Synthesised perovskite

Compounds	2θ			θ			**Cell dimension**	**Cell Angle**	**Cell Volume**	**Shape of Crystal**
	Peak 1	Peak 2	Peak 3	Peak 1	Peak 2	Peak 3				
Perovskite	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL

XRD spectrum of the synthesised perovskite showed the absence of any crysttainne structure with no defined peak revealing the amorphous structure (Dantio et al., 2021).

Effects of Experimental Variables

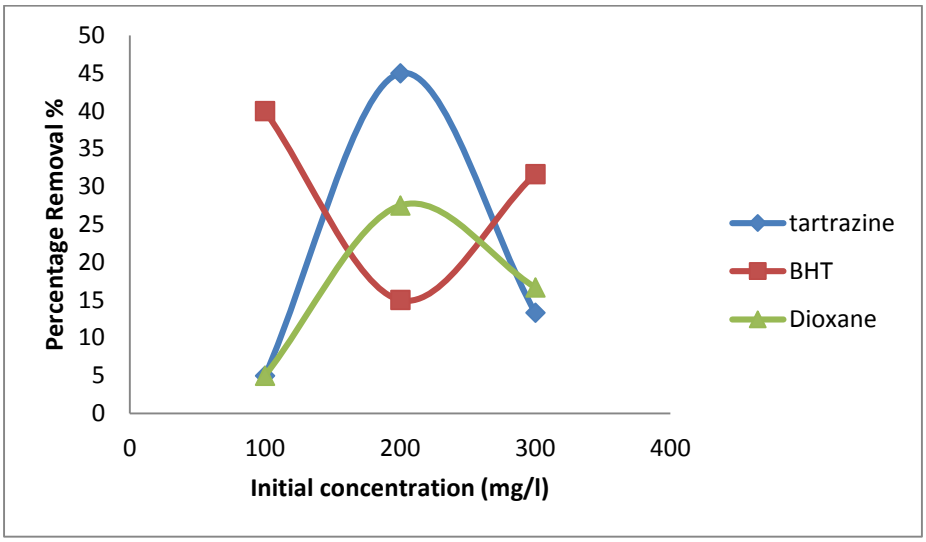


Fig 1 Effect of initial concentration on percentage removal of the pollutants using the perovskite ($ZrCoO_3$)

The effect of initial concentration on the adsorption of tartrazine, BHT and dioxane onto perovskite was studied in the range of 100 mg/l to 400 mg/l and is shown in Fig 1 It could be observed that the percentage removal of tartrazine and dioxane increased with increase in initial concentration while the percentage removal of BHT decreased with increase in initial concentration. This is due to the fact that increase in adsorbate concentration will make more adsorbate available for adsorption, while the decrease in percentage removal with increase in initial concentration was as a result of the saturation of the active sites at higher concentration (Dantio et al., 2021).

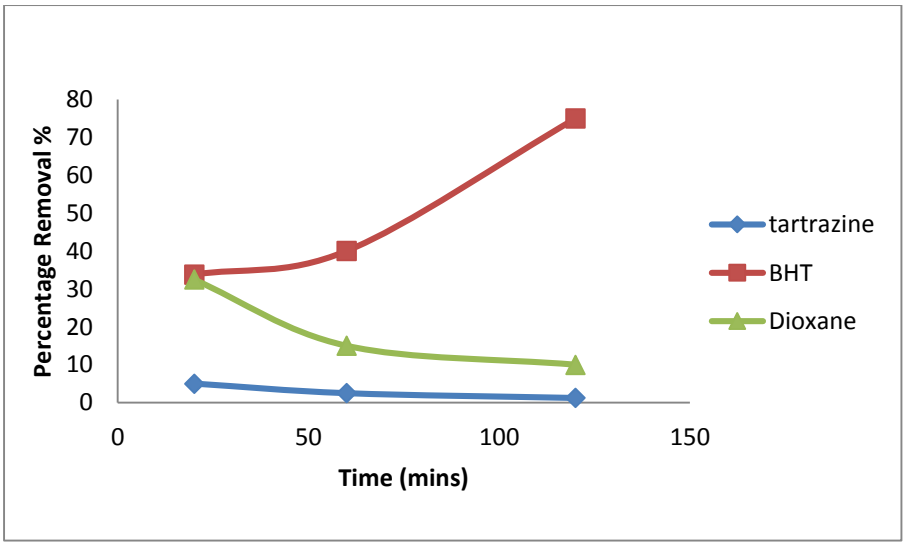


Fig 2 Effect of contact time on percentage removal of the pollutants using the perovskite ($ZrCoO_3$)

The effect of contact time on the adsorption of tartrazine, BHT and dioxane onto perovskite was studied between the intervals of 20-120 minutes and is shown in Fig 2. It could be observed that there was slow increase in percentage removal of BHT as the contact time increases from 20-60 minutes after which the increase became rapid from 60-120 minutes which was as a result of

overcrowding of the active site as time increases. It can also be observed that there was a decrease in percentage removal of tartrazine and dioxane from 20-60 minutes after which the decrease proceeded slowly from 60- 120 minutes which is due to unsaturated active site (Dantio et al., 2021).

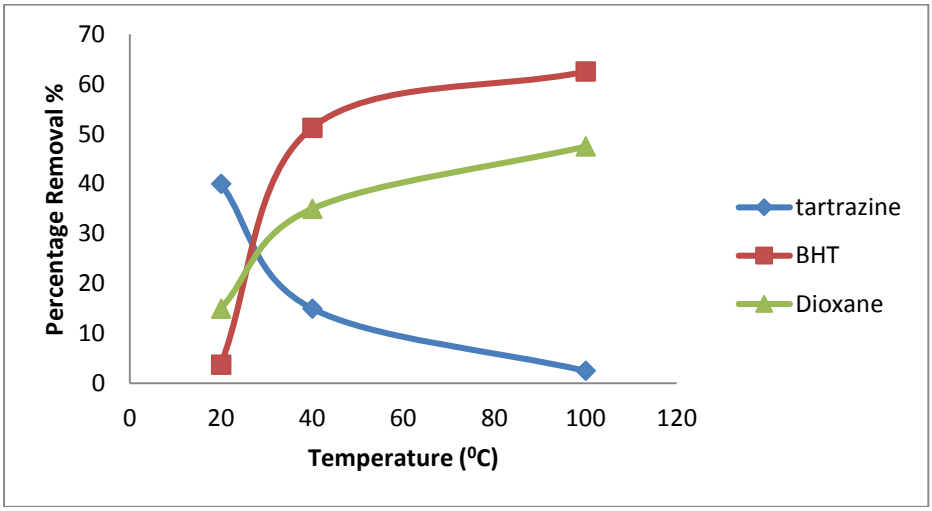


Fig 3 Effect of temperature on percentage removal of the pollutants using the perovskite ($ZrCoO_3$)

The influence of temperature on the percentage removal of tartrazine, BHT and dioxane by perovskite is shown in Fig 3 It could be observed that increase in temperature resulted in decrease in percentage removal of tartrazine while it resulted to increase in percentage removal of BHT and dioxane. The decrease in removal efficiency with increase in temperature could be attributed to the weakening of the physical bonding between the adsorbate and the active sites of the adsorbent. While the increase in percentage removal of BHT and dioxane with increase in temperature is as a result of the endothermic nature of the reaction (Enenebeaku et al., 2016).

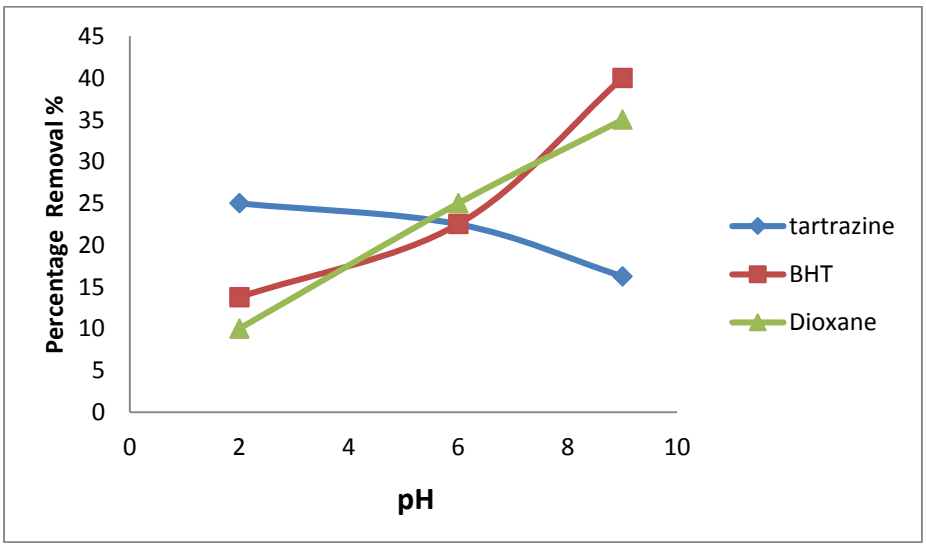


Fig 4 Effect of pH on percentage removal of the pollutants using the perovskite $ZrCoO_3$)

The influence of pH on the adsorption of tartrazine, BHT and dioxane onto perovskite is shown in Fig 4. It could be observed that the percentage removal of BHT and dioxane increased as pH increased, while the percentage removal of tartrazine decreased as pH increased. This could be

attributed to the fact that at high pH values of the solution, the presence of excess hydroxyl ion in the solution competes with the anionic groups of the adsorbates for the adsorption sites on the adsorbent surface. While at low pH values, the negative charges (OH^-) in the solution decreases and the adsorbent surface is more positively charged, thus enhancing attraction of more amounts of the anions of the adsorbates (Enenebeaku et al., 2016).

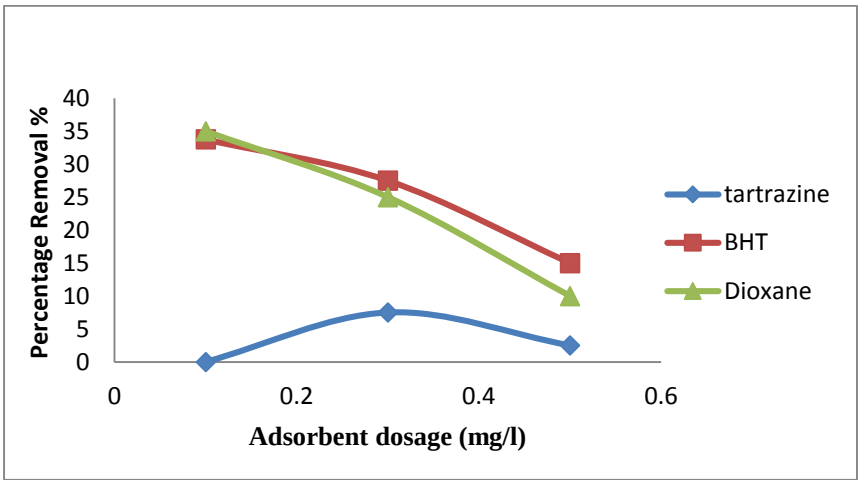


Fig 5 Effect of adsorbent dosage on percentage removal of the pollutants using the perovskite ($ZrCoO_3$).

The effect of adsorbent dosage on the percentage removal of tartrazine, BHT and dioxane by perovskite is shown in Fig 5. It could be observed that the percentage removal of BHT and dioxane decreased with increase in adsorbent dosage while that of tartrazine increased with increase in adsorbent dosage. The increase in percentage removal of tartrazine as adsorbent dosage was as a result of increase in the number of active sites on pervoskite surface with the increase in the adsorbent dosage. After a while, the percentage removal of tartrazine started to decrease as the adsorbent dosage increases. This may be due to aggregation of the adsorption sites which limits the availability of all the active sites during adsorption process (Chukwuemeka-Okorie et al., 2021).

Adsorption Isotherm

Langmuir isotherm

The most widely used isotherm equation (Amin NK 2009) for modeling of the sorption equilibrium data is the Langmuir isotherm. The linear form of langmuir isotherm equation is given by the equation (Langmuir 1918)

$$C_e/q_e = 1/q_mK_L + C_e/q_m \quad (1)$$

where, C_e is the equilibrium concentration of the dye (mg/L), q_e is the amount of dye adsorbed per unit mass of AC (mg g^{-1}), q_m and K_L are langmuir constants related to adsorption capacity and rate of adsorption, respectively. The langmuir constants was evaluated from the slope and the intercept of linear equation (Table 5). The correlation coefficients of langmuir isotherms, R^2 are 0.094, 0.179 and 0.003 for P+T, P+B, P+D respectively. The values of R^2 were found to be <1 for all the adsorptions suggesting the isotherm to be favorable at the concentrations studied (El-Sayed GO 2010).

Freundlich isotherm

This model can be represented by:

$$\ln q_e = \ln K_f + 1/n \ln C_e \quad (2)$$

where, K_f (mg/g) and n are freundlich constants.
To compare the langmuir and freundlich isotherm models. It could be seen (Table 6) that the obtained data fit better to the freundlich model than the langmuir model which implies that the adsorption is of heterogenous adsorption surface with unequal available sites with different energies of adsorption (Amin NK 2008). The langmuir and freundlich isotherm plots are shown in Figures 6 and 7 respectively.

Table 5 Evaluation for Langmuir isotherm model

Langmuir parameters	Perovskite		
	P+T	P+B	P+D
Slope	0.307	0.125	0.01
Intercept	136.7	12.89	46.01
q_m(mg/g)	3.257329	8	100
K_L(L/mg)	0.002246	0.009697	0.000217
R^2	0.094	0.179	0.003

Table 6 Evaluation for Freundlich isotherm model

Freundlich	Perovskite		
	P + T	P + B	P + D
Slope	1.025	0.372	1.111
Intercept	-4.099	-0.227	-4.296
K_f	0.0166	0.7969	0.0136
N	0.97561	2.688172	0.90009
R^2	0.139	0.168	0.685

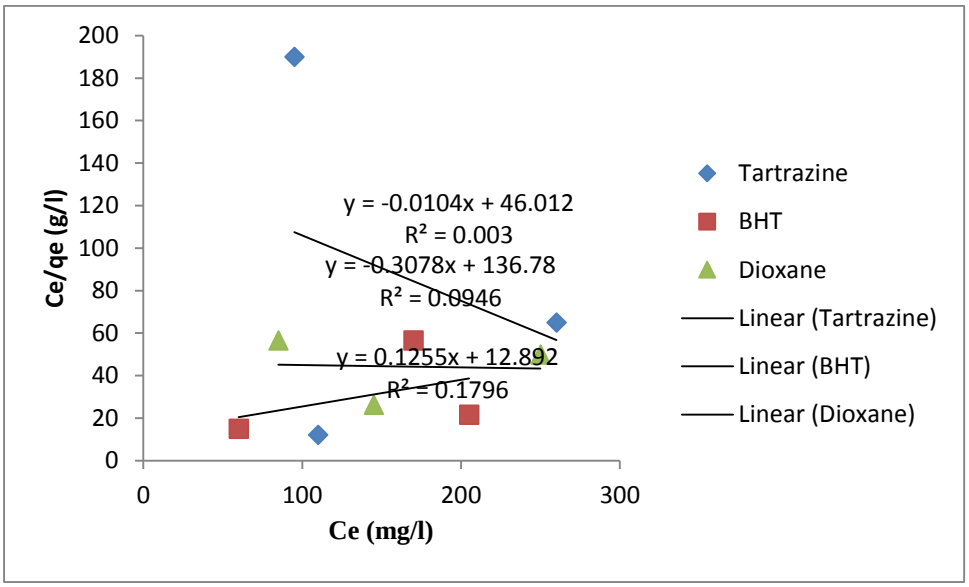


Fig 6 Langmuir Isotherm plot for adsorption of tartrazine, BHT and dioxane onto the perovskite ($ZrCoO_3$)

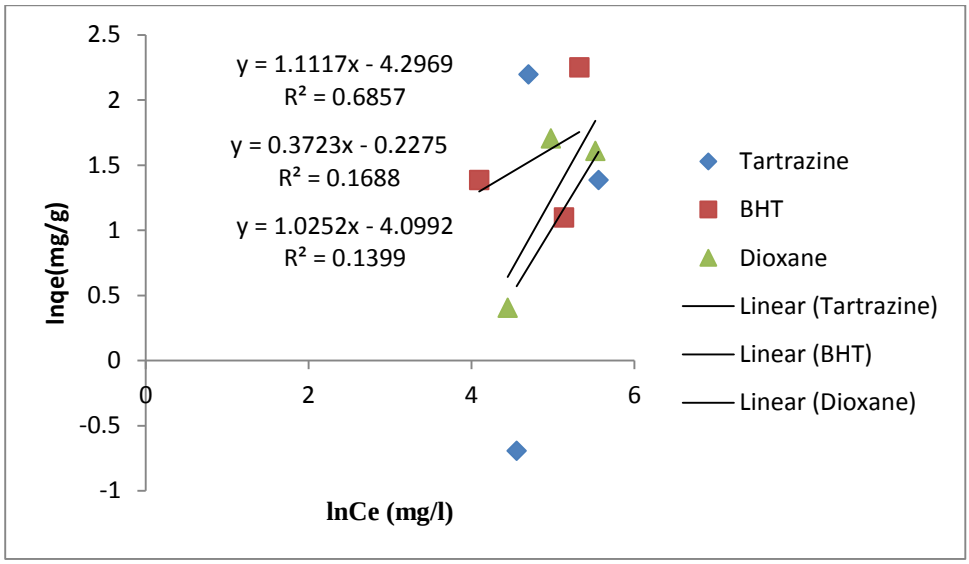


Fig 7 Freundlich Isotherm plot for adsorption of tartrazine, BHT and dioxane onto the perovskite ($ZrCoO_3$)

Adsorption Kinetics

Pseudo-First Order Model

From the graph of the pseudo-first order kinetics in Figure 8 it was observed that the relationship between In(qe-qt) and time is not linear which confirms it does not obey a pseudo-first order model for P+T, P+B and P+D as shown in Table 6. The value of coefficient of determination R^2 and other values indicate that Pseudo-first order model did not provide a good description for adsorption of tartrazine, BHT and dioxane unto Ferrite.

Table 7 Evaluation for pseudo first order model

Pseudo 1st order	Perovkite		
	P + T	P + B	P + D
Slope	0.022	0.01	0.028
Intercept	-0.726	0.375	-1.417
qe.cal(mg/g)	0.4838	1.4505	0.2424
K_1(/min)	-0.022	-0.01	-0.028
R^2	0.415	0.45	0.628

Pseudo-Second Order Model

Arising from the plot of the pseudo-second order kinetics, it is evident that the relationship between t/qt and t is linear which confirms the model. From the value of coefficient of determination R^2, it is evident that pseudo-second order model provides a better interpretation for the adsorption process, better than the pseudo-first order model model which suggests that the mass transfer mechanisms were important factors in the uptake of the adsorbates on the adsorbents and that chemisorption may be the rate determining step for the sorption process (Chukwuemeka-Okorie et al., 2021).

Table 8 Evaluation for pseudo second order model

Pseudo second order	Perovskite		
	P + T	P + B	P + D
Slope	23.55	0.235	2.884
Intercept	-536.8	15.08	-53.84
h (mg/gmin)	-0.00186	0.066313	-0.01857
K_2 (g/mgmin)	-1.03316	0.003662	-0.15448
qe(mg/g)	0.042463	4.255319	0.346741
R^2	0.96	0.728	0.986

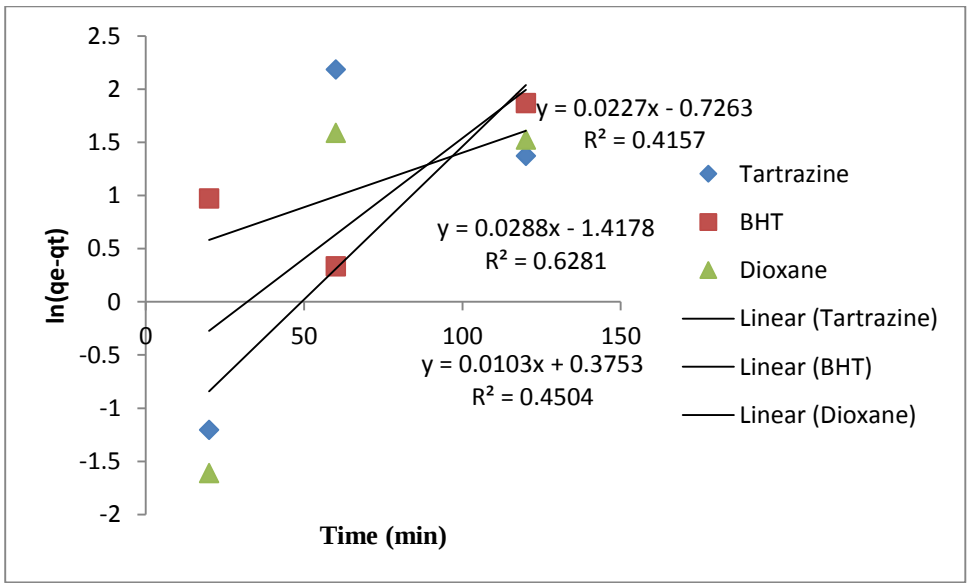


Fig 8 Pseudo first order plot for adsorption of tartrazine, BHT and dioxane onto the perovskite ($ZrCoO_3$)

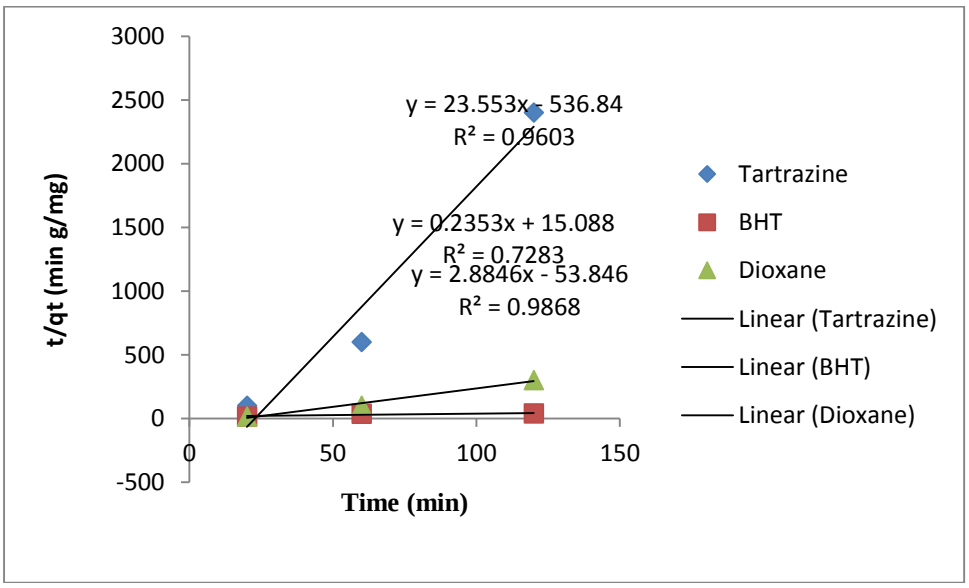


Fig 9 Pseudo first order plot for adsorption of tartrazine, BHT and dioxane onto the perovskite ($ZrCoO_3$)

Adsorption Thermodynamics

Thermodynamic parameters such as change in free energy ΔG°(kJ/mol), enthalpy ΔH° (kJ/mol) and entropy ΔS° (J/K/mol) were determined. ΔG° was calculated from the following equation (Gupta et al., 2003):

$$\Delta G = -RT \ln k \quad (3)$$

where: K_L is the Langmuir constant; T is absolute temperature and R is the gas constant (8.314 J/mol K). The apparent ΔH° and ΔS° were calculated from adsorption data at different temperatures using the Van't Hoff equation (Namasivayam C and Kavitha D., 2002):

$$\ln K_L = \Delta S/R - \Delta H/RT \quad (4)$$

where: K_L is the Langmuir constant and T is the solution temperature (K).The magnitude of ΔH^o and ΔS^o was calculated from the slope and intercept from the plot of ln K_L vs 1/T (Fig 10). The calculated thermodynamic parameters are given in Table 8. It is known that physical adsorption and chemisorptions can be classified, to a certain extent, by the magnitude of the enthalpy change. It is accepted that bonding strengths of <40 kJ/mol are typically those of physical adsorption type bonds. Chemisorption bond strengths can range from 40 to 120 kJ/ mol (Alkan et al.,2004). Based on this, the adsorption of tartrazine, BHT and dioxane appeared to be physical adsorption process, the energy of adsorption in the range of physisorption lends credence to its potential in catalytic applications and possible breakdown of pollutants. The negative value of ΔS^o for adsorption of tartrazine indicate the decrease in randomness at the solid/liquid interface during the adsorption process, while the positive values of ΔS^o for adsorption of BHT and dioxane indicate the increase in randomness at the solid/liquid interface during the adsorption process. The adsorption of tartrazine, BHT and dioxane were non spontaneous for the adsorption at the temperatures under investigation as indicated from the positive values of free energy (ΔG^o).

Table 9 Evaluation for ΔG^o (KJ/mol)

Thermodynamics		Perovskite		
		P + T	P + B	P + D
ΔG^o	Temp (K)			
	293	6.9958	11.1713	9.1473
	333	12.8598	7.7353	8.1113
	393	21.6558	2.5813	6.5573

Table 10 Evaluation for thermodynamic parameters

	Perovskite		
	P + T	P + B	P + D
Slope	4325	-4371	-2013
Intercept	-17.63	10.33	3.113
ΔS(KJ/mol)	-0.1466	0.0859	0.0259
ΔH(KJ/mol)	-35.958	36.340	16.736
R^2	0.984	0.643	0.82

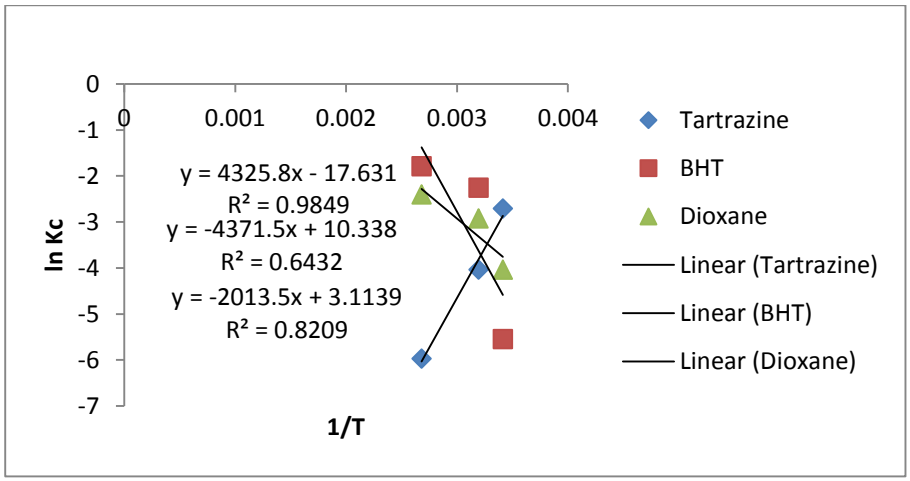


Fig 10 Van't Hoff plot for adsorption of tartrazine, BHT and dioxane onto Perovskite

Conclusion

Mixed metal oxide nanoparticle, perovskite was synthesised. The physical properties of the synthesised mixed metal oxide were determined. Characterisation was done by FTIR and XRD. It was used for adsorption of tartrazine, BHT and dioxane from aqueous environment through batch adsorption. FTIR spectra indicated ten adsorption bands at 693.28484cm^{-1}, 838.65101cm^{-1}, 1021.29057cm^{-1}, 1148.02005cm^{-1}, 1401.47903cm^{-1}, 1561.75455cm^{-1}, 1871.12359cm^{-1}, 2109.67322cm^{-1}, 2366.85953cm^{-1}, 3186.87385cm^{-1}, 3548.42562cm^{-1} indicating the presence of aromatic compound, halo compound, vinyl ether, aliphatic ether, sulfone, nitro compound, anhydride, isothiocyanate, carbondioxide, carboxylic acid and alcohol respectively. XRD spectra showed no peak revealing that the synthesised perovskite is not crystalline but amorphous. Various parameters such as contact time, adsorbent dosage, initial ion concentration, pH and temperature were studied to observe their effect in the adsorption process. The experimental equilibrium adsorption data fitted more to freundlich than langmuir isotherm model. From the kinetic data it was evident that pseudo-second order model provided better interpretation for the adsorption process than the pseudo-first order model. Thermodynamic quantities such as Gibbs free energy, enthalpy and enthropy were evaluated. The adsorption of tartrazine, BHT and dioxane were non spontaneous for all the adsorption at the temperatures under investigation. This research shows that the adsorption of tartrazine, BHT and dioxane depended on time, pH, adsorbent dosage and temperature and this mixed metal oxide can be used as effective adsorbent for the removal of contaminants from aqueous environment.

References

Alkan, M., Demirbaş, O., Celikçapa, S., & Doğan, M. (2004). Sorption of acid red 57

Amin, N. K. (2008). Removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from sugarcane bagasse pith. *Desalin* 223,152-161.

Amin, N. K. (2009). Removal of direct blue-106 dye from aqueous solution using new activated carbons developed from pomegranate peel: adsorption equilibrium and kinetics. *Journal of Hazard Mater*. 165, 52-62.

Burton, G. W., & Ingold, K. U. (1981). Autoxidation of biological molecules. 1. Antioxidant activity of vitamin E and related chain-breaking phenolic antioxidants in vitro. *Journal of the American Chemical Society, 103*(21): 6472–6477. doi:10.1021/ja00411a035

Chen, N., Zhang, Z., Feng, C., Zhu, D. Y., Yang, Y., & Sugiura, N. (2011). Preparation and characterisation of porous granular ceramic containing dispersed aluminium and iron oxide as adsorbents for fluoride removal from aqueous solution. *J. Hazard. Mater*., 186, 863-868.

Chukwuemeka-Okorie, H.O., Ekuma, F. K., Akpomie, K. G., Nnaji, J.C., & Okereafor, A.G. (2021). Adsorption of tartrazine and sunset yellow anionic dyes onto activated carbon derived from cassava sievate biomass. *Applied Water Science,11(27):*3-6 https:/doi.org/10.1007/s13201-021-01357-w

Corma, A. (1995). Inorganic solid acids and their use in acid catalyzed hydrocarbon reactions. *Chem. Rev.* 95, 559–614.

Dantio, N. C., Ngomom, H. M., Benedoue, S. A., Kouotou, D., Abega, A. V., Ndong, N. A., Che, R. N., Julius, N. (2021). Adsorption of tartrazine onto activated carbon based cola nuts shells: Wquilibrium, kinetics and thermodynamics studies. *Open Journal for Inorganic Chemistry*, 11, 1-19.

El-Sayed, G. O. (2010). Removal of water hardness by adsorption on peanut hull. *Journal of International Environmental Science,* 5, 47-55.

Enenebeaku, K. C., Okorocha, J.N., Enenebeaku, E.U., Anukam,B., Onyeocha,O.V., Ogukwe, E.C & Oguzie, E.E.(2016). Adsorption of congo red dye from aqueous solution using agricultural waste.*Journal of Applied Chemistry*: 9(9). 39-51.

Gan, L. M., Zhang, L. S., Chan, H. S., Chew, C. H., & Loo, B. H. (1996). A novel method for the synthesis of perovskite-type mixed stability. *European Journal of Lipid Science and Technology*, *119* (11): 1600343. doi:10.1002/ejlt.201600343.

Gupta, V., Ali, K., Suhas, I., & Mohan, D. (2013). Equilibrium uptake and sorption dynamics for the removal of a basic dye (basic red) using low-cost adsorbents. *J Colloid Interface Sci* 265, 257-264.

Heinz, D., Hoelderich, W. F., Krill, S., Boeck, W., & Huthmacher, K. (2000). V_2O_5/TiO_2 catalysts for the vaporphase oxidation of b-picoline: Influence of the TiO2 carrier. *J. Catal.* 192, 1–10.

Kiessling, D., Went, G., Hagenau, K., & Schoellner, R. (1991). Dimerization of n-butenes on amorphous nickel oxide–alumina/silica catalysts. *Appl. Catal.* 71, 69–78.

Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, micaand platinum. *J Am Chem Soc*, 40, 1361-1403.

Menkiti, M. C., Aneke, M. C., Ejikeme, P. M., Onukwuli, O. D and Menkiti, N.U. (2014).*Adsorptive treatment of brewery effluent using activated chrysophyllumalbidum seed shell carbon.*Retrieved fromhttp://www.springerplus.com/content/3/1/213, onSeptember 15,2019.

Monshi, A., & Attar, S. (2009). A new method to measure nanosized crystals by Sherrer equation using XRD.*Majlesi Journal of materials Engineering*: 2(6), 9-18.

Namasivayam, C., & Kavitha, D. (2002). Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. *Dyes Pigm*, 54, 47-58.

Pate, L. N., Khan, M. D., Shahane, S., Rai, D., Chauhan, D., Kent, C., & Chaudhavy, V. K. (2020). Emerging pollutants in Aquatic Environment: Sources, effects and challenges in biomonitoring and bioremediation. *A Review Pollution*, *6*(1),99-111. http://doi 10.22059/poll.2019. 285116.646

Reddy, B. N., & Subrahmanyam, M. (1992). Ammoxidation of 3-picoline over highly dispersed vanadia on alumina–silica mixed support. *Langmuir*, 8, 2072–2073.

Sajan, B., Reshma, R., Komal, B., & Abaji, G. (2015). The Applications of Mixed Metal Oxides to Capture the CO_2 and Convert to Syn-Gas" Bulletin of Chemical Reaction Engineering & Catalysis, *10*(2), 125-142.

Sumanjit, S., Walia, T. P., & Ravneet, K. (2007). Removal of Health Hazards Causing Acidic Dyes from Aqueous Solutions by the Process of Adsorption. *Online Journal of Health and Allied Sciences*, *6*(3) 1-10.

Watanabe, H., & Koyasu, Y. (2000). New synthesis route for Mo–V–Nb–Te mixed oxide catalyst for propane ammoxidation. *Appl. Catal. A*, 194–195, 479–485.

Weil, R. R & Brady, N. C. (2016).The nature and properties of soils, *Columbus: Pearson*: 15(1).23.

Yehye, W. A., Rahman, N. A. Ariffin, A., Hamid, S. B., Alhadi, A. A., Kadir, F. A., & Yaeghoobi, M. (2015). Understanding the Chemistry behind the antioxidant activities of Butylated Hydroxytoluene (BHT): A Review. *European Journal Medical Chemistry*, 101, 295–312. doi:10.1016/ j.ejmech.2015.06.026

Yogesh, C. S. (2012). A guide to the economic removal of metals from aqeous solutions. New Jersey and Massachusetts: Wiley and Sons Inc. and Scrivener Publishing LLC.

Zenker, M. J., Borden, R. C., & Barlaz, M. A. (2003). Occurrence and Treatment of 1,4-Dioxane in Aqueous Environments. *Environmental Engineering Science*, 20, 423- 432.