# CHARACTERIZATION AND MODIFICATION OF NATURAL CLAY DEPOSITS TO DEVELOP CLAY-BASED ADSORBENT TO REMOVE PHOSPHORUS FROM CONTAMINATED WATER

by

# **Farzana Nargis**

B.Sc. in Chemical Engineering, Bangladesh University of Engineering and Technology, 2017

# THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN NATURAL RESOURCES AND ENVIRONMENTAL STUDIES (ENVIRONMENTAL SCIENCE)

UNIVERSITY OF NORTHERN BRITISH COLUMBIA

August 2021

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# Abstract

Modification of natural clays may be a useful approach to produce an effective and low-cost adsorbent to control phosphorous, which is a key factor in controlling the eutrophication of surface waters. In this study, natural clay samples were collected, characterized, modified with ZrCl4, and then their adsorption capacity for removing phosphorus from contaminated water was studied. XRD analysis showed that the natural clay consists of kaolinite, illite, and nontronite as dominant clay mineral phases. The maximum adsorption capacity of the modified clay increased from 0.493 to 11.83 mg P/g compared to the unmodified clay. The adsorption process was fast for both natural and modified samples, achieving more than 80% and 90% phosphorus removal with natural and modified samples, respectively in less than 4 hours. The adsorption data for both clays best fit the Langmuir isotherm, and the rate of phosphorus adsorption was found to follow a pseudo-secondorder kinetic model. The adsorption capacity of both adsorbents decreased with increasing pH, and for the modified clay the change was more significant. Full factorial design and response surface methodology were applied to evaluate and optimize the effects of initial P concentration, contact time, pH, and dose. From the model, the maximum P removal efficiency predicted for the synthetic solution was 91.5% and 99.9% by natural and modified clay, respectively.  $R^2 \approx 0.98$  indicates that the observed results fitted well with the model prediction. Similar to the batch studies, the fixed bed column study showed the developed adsorbents are efficient in removing phosphorus from water in a continuous process as well.

Keywords: Eutrophication; Clay; Phosphorus adsorption; Factorial design; Optimization

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# List of Abbreviations and Symbols

ANOVA	Analysis of variance
ATR-FTIR	Attenuated Total Reflectance – Fourier-Transform Infrared (spectroscopy)
BET	Brunauer-Emmett-Teller
Ce	The equilibrium concentration of the adsorbate
DF	Degree of freedom
DOE	Design of Experiment
IC	Ion Chromatography
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
$K_{\rm f}$	Freundlich adsorption isotherm constant
K <sub>L</sub>	Langmuir adsorption isotherm constant
K <sub>YN</sub>	Yoon-Nelson model proportionality constant
MS	Mean squares
NC	Natural clay
qe	Adsorption capacity at equilibrium
Qm	Maximum adsorption capacity
$\mathbb{R}^2$	Coefficient of determination
RSM	Response Surface Methodology
SA	Sodium Alginate
SD	Standard deviation
SEE	Standard Error of the Estimate
SEM	Scanning Electron Microscope
SS	Sum of the squares
TGA	Thermogravimetric Analysis
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
ZrMC	Zirconium modified clay
τ	50% adsorbate breakthrough time

# Acknowledgements

Firstly, I would like to thank Almighty Allah for giving me strength and patience throughout these years to attain my goals for the successful completion of graduate studies. Then, I would like to express my gratitude towards my supervisor Dr. Hossein Kazemian for his constant support and guidance and for accepting me into his group. I feel lucky and blessed to have a supervisor like him who is energetic, helpful, and caring at the same time. I was always motivated by my supervisor because of his dedication and passion for research. I would also like to express my gratitude to my supervisory committee members Dr. Mike Rutherford, and Dr. Jianbing Li, for their feedback throughout my project. I also would like to thank Mitacs, Mindbody Network Inc., and the UNBC office of Research for funding this project.

Also, I am very much grateful to the analytical specialists Erwin Rehl and Charles Bradshaw at the Northern Analytical Lab Service (NALS), for their cooperation during the sample measurement and data analysis. In addition, I am thankful to Ann Duong and Mya Schouwenburg at NALS for their help during my research work.

I also want to say thanks to Mostafa Marzi, a visiting.Ph.D student at UNBC from Iran, for his great support and motivation towards my research. I am also very much thankful to all my friends at UNBC, specially Simisola Idim, Sahar Ebadzadsahraei, Dorna Sobhani, Navjot Kaur, Mandeep Kaur, Lon Kerr, for being with me whenever I needed them!

Finally, my heartfelt appreciation goes to my husband and friend M Bakhtiar Azim; without his inspiration, I would not be able to attain this height. I also would like to express my deepest gratitude to my parents, sister, and brother in Bangladesh for their continuous support, encouragement, and blessings.

# **1** Introduction

#### **1.1 Background of the study**

Phosphorus (P) is an essential element for both plant and animal growth and to maintain profitable crop and livestock production, for which one of the most important uses of phosphorus is in the manufacture of ammonium phosphate fertilizers (Savci, 2012). It also plays a vital role during the production of steel, special glasses, fine chinaware, and detergents (Nosenko et al., 2008). Along with being a critical nutrient for growth and food production, P in excessive amounts in soils from fertilizer application, livestock manure, and wastewater runoff are leaching into downstream freshwater ecosystems, which causes eutrophication and overgrowth of nuisance plant species and algae by increasing the biological productivity of surface waters (Boeykens et al., 2017). Although eutrophication is a natural process, it may be accelerated by increasing the quantity of nutrients supplied to an aquatic system (Mateus and Pinho, 2010). The Environmental Protection Agency has identified eutrophication as the main problem in the United States surface waters that have impaired water quality (Nutrient Pollution, 2019). Similarly, according to a Canadian national watershed report by WWF (2017), 42 of the 67 sub-watersheds with known water quality data in Canada have "fair" or "poor" water quality. Effects of nutrient overloading in lakes range from increased biomass to composition change in aquatic food webs, to decreases in water transparency and oxygen levels, to declining fish populations, to toxic algal blooms that can cause death in animals and health issues in humans (Smith et al., 1999). Nitrogen and phosphorous both affect eutrophication, but phosphorus has been cited as a vital and limiting nutrient in freshwater systems. Several studies have indicated that a phosphate concentration as low as  $0.02 \text{ mg L}^{-1}$  in a water reservoir is sufficient to stimulate algal growth (Kilpimaa et al., 2015) and suggested that a decrease in phosphorus can effectively control eutrophication in coastal and freshwater systems (Smith, 2003). Therefore, phosphorous discharged from municipal and industrial wastewater treatment plants must be controlled to limit the eutrophication of surface waters. This research was conducted with an aim to remove phosphorus from water with low cost but highly efficient clay adsorbents.

## **1.2** Literature Review

Clays are inherently occurring fined-grained minerals ( $\leq 2 \mu m$ ) that become plastic when wet and hard when dried or fired (Guggenheim and Martin, 1995). Clay minerals refer to the family of phyllosilicates minerals and are characterized by platy morphology due to the arrangement of atoms in their structure (Bergaya and Lagaly, 2006). These minerals are differentiated by the presence of layered polymeric silicate tetrahedral sheets linked to Al, Fe, or Mg oxide octahedral sheets (Ismadji et al., 2015). They are formed by chemical weathering actions involving other silicate-containing minerals found on the earth's surface. These low-cost minerals are among the most important industrial minerals because of their high sorption properties and potential for ion exchange. For these unique properties, they are being used as adsorbents, ion exchangers, supports, catalysts, paper coatings, ceramics, pharmaceuticals, and many other industries (Murray, 1991). These versatile applications of the clay minerals depend on their very small size with large specific surface area, different layered structure, and the possibility of modifying their surface to increase their affinity for anions and organic molecules structure as well as their mineralogical and chemical composition. However, the number of research on phosphate or phosphorus absorption is quite limited, with the majority of them focusing on bentonite, montmorillonite, palygorskite, and kaolinite (Bacelo et al., 2020). An understanding of clays and clay based-mineral properties is fundamental to their effective usage in adsorption applications. Most clays have a net negative charge, making them good adsorbents for metal and organic cations but not very efficient for phosphate (Bacelo et al., 2020). Therefore, modification is suggested to improve adsorption capacity by enhancing the surface area through its effect on the surface and micropore structure of the clay (Perassi and Borgnino, 2014, El Bouraie and Masoud, 2017). Modification of clay could occur by adding a metallic ion or through heat and acid treatment, among others. Thus, numerous researchers have modified the surface of adsorbents to achieve better P removal from wastewater.

Several laboratory experiments and articles have demonstrated that oxides and hydroxides of different metals, such as Al (Genz et al., 2004, Tanada et al., 2003); Zr (Liu et al., 2008, Chitrakar et al., 2006); Mn (Mustafa et al., 2006); Fe (Long et al., 2011); La (Tian et al., 2009) can be applied to remove phosphate from contaminated water, because of the high specific affinity and adsorptive selectivity between phosphorus-based ions and these metal sites. However, using pure metal oxides/hydroxides as adsorbents in removing phosphate from water on large scale is not economical as well as the metal oxide particles lack the mechanical strength necessary for longterm operation in fixed-bed systems when employed in their native form. As a result, a supporting material or structure that can hold an accessible, functional dispersion of metal oxide particles for phosphate adsorption is required. Natural clay minerals can be used for this purpose because of their abundance, large availability, low cost as well as their layered structure, chemical and mechanical stability, large specific surface area, and pore spaces. Therefore, researchers have shown a lot of interest to modify different low-cost natural minerals with the addition of metallic ion through different type of treatments to improve the adsorption capacity. Moharami & Jalali investigated P removal adsorption from aqueous solution with FeCl<sub>3</sub>, CaCl<sub>2</sub>, and NaCl modified bentonite and kaolinite clay, and among them, the maximum sorption capacity of P was obtained by Fe modified adsorbents. After Fe modification, the P sorption capacity of both adsorbents increased in the range from 0.28 to 1.31 mg P/g. Another study (Huang et al., 2015) suggested that

Zr-Al modified montmorillonite can be utilized as a potentially effective phosphate adsorbent for practical applications. Some other recent research has investigated phosphate/phosphorus adsorption on different natural and modified clays from different contaminated sources, for example, on aluminum-modified clay from a heavily polluted lake (Yang et al., 2020); onto chemically modified carbonaceous clay from contaminated lake water (Selim et al., 2019); on red mud clay from contaminated water (Gładysz-Płaska et al., 2018); on hydroxyapatite-bentonite clay-nanocellulose composite from aqueous solution (Hokkanen et al., 2018). Ye et al. reported, employing an acid treatment followed by calcination to palygorskite, the adsorption capacity increased from 3.8 to 8.3 mg P/g (Ye et al., 2006). El Bouraie and Masoud proposed the modification of bentonite with Mg(OH)<sub>2</sub>, which led to the formation of clusters between the interlayer spaces, improvement of surface area, and increase in phosphate adsorption capacity (El Bouraie and Masoud, 2017). Yan et al. proposed the use of hydroxy-aluminum, hydroxy-iron, and mixed hydroxy-iron-aluminum pillared bentonites where the maximum adsorption capacities for Al-bentonite, Fe-bentonite, and Fe-Al-bentonite were obtained 12.7, 11.2, and 10.5 mg P/g, respectively (Yan et al., 2010). Another study stated that the adsorption capacity of bentonite to remove phosphate increased from 14 to 18 mg/g with 10% Al<sub>2</sub>O<sub>3</sub> addition (Osalo et al., 2013). To examine the adsorption characteristics of calcite-coated phyllosilicates, Perassi and Borgnino treated montmorillonite with CaCO<sub>3</sub> and found higher adsorption capacity with the modified clay (Perassi and Borgnino, 2014). Tian et al. observed that adsorption capacity increased from 6.67 to 8.9 mg/g when lanthanum was combined with aluminum during pillaring during the modification process of natural clay (Tian et al., 2009). Similar results were obtained by Huang et al., where Zr-Al pillared montmorillonite showed better performance in removing phosphate from water (Huang et al., 2015). Selim et al. reported chemically modified carbonaceous clay with cetylpyridinium chloride was able to increase the phosphate adsorption capacity from 10.915 to 21.364 mg/g (Selim et al., 2019).

Phosphate removal by clay-based adsorbents has primarily been described as ligand exchange or precipitation processes (Goldberg and Sposito, 1985, Namasivayam and Prathap, 2005, Zhou et al., 2010). Ligand exchange happens when anions in hydroxylated minerals with a specific affinity for metal ions are absorbed out of proportion to their concentration in aqueous solutions (Goldberg and Sposito, 1985). In ligand exchange, hydroxyl groups on clay metal ions are exchanged with phosphate ions in an aqueous solution, allowing the phosphate ions to be captured by creating an inner-sphere complex on the clay surface while the hydroxyl ions are released into the solution. (Zhu and Zhu, 2007). The ligand exchange mechanism is indicated by an increase in the pH of the solution caused by the release of hydroxyl ions. When no water is held between the surface Lewis acid sites, the surface complexes produced via ligand exchange are referred to as inner-sphere complexes. Phosphate ions are held by covalent or ionic bonds (Goldberg and Sposito, 1985), and are represented in Equations 1 and 2:

$$\equiv \mathbf{M} - \mathbf{O}\mathbf{H} + \mathbf{H}_2 \mathbf{P} \mathbf{O}_4^- \leftrightarrow \equiv \mathbf{M} - (\mathbf{H}_2 \mathbf{P} \mathbf{O}_4) + \mathbf{O}\mathbf{H}^- \tag{1}$$

$$2 \equiv M-OH + HPO_4^{2-} \leftrightarrow M_2 - (HPO_4) + 2OH^-$$
(2)

Outer sphere complexes are formed by electrostatic attraction with water retained between the ligand and the exchange sites; the reaction is represented as Equations 3 and 4:

$$\equiv \mathbf{M} - \mathbf{O}\mathbf{H}_2 + \mathbf{H}_2 + \mathbf{P}\mathbf{O}_4^- \leftrightarrow \equiv \mathbf{M} - (\mathbf{O}\mathbf{H}_2^+) (\mathbf{H}_2\mathbf{P}\mathbf{O}_4^-)$$
(3)

$$\equiv \mathbf{M} - \mathbf{OH}_2^+ + \mathbf{HPO}_4^{2-} \leftrightarrow \equiv \mathbf{M} - (\mathbf{OH}_2^+) (\mathbf{HPO}_4^{2-}) \tag{4}$$

Another mechanism in which clay-based minerals remove phosphorus/phosphate from wastewater is precipitation. Phosphate precipitation takes place when the solubility of the product of the precipitate is exceeded by the product of the solution concentrations of the components of the precipitate (Loganathan et al., 2014).

# **1.3 Research Aim and Objectives**

The aim of this research was to characterize unknown natural clay samples and develop a claybased adsorbent to remove phosphorus from wastewater, maximize the phosphorus adsorption capacity of the adsorbent and determine the suitability of the use of the adsorbent in a fixed bed column study.

The specific objectives of this research will be to:

- 1. Identify the physical, chemical and mineralogical characteristics of the clay samples.
- 2. Modify the natural clay with Zirconium (IV) Salts.
- 3. Investigate the predominant phosphorus removal by the natural and modified clay and study the Adsorption Isotherm and Kinetics.
- 4. Study the effect of different process parameters such as pH, contact time, adsorbent dose, initial phosphorus concentration on the adsorption process and thus understand the adsorption mechanism involved in the process.
- 5. Determine the optimum condition of the adsorbents to optimize phosphorus removal from aqueous solution by developing the full factorial design of batch experiment and statistical analysis.
- 6. Investigate the performance of the natural and modified clay at the optimized condition in a continuous flow column and its applicability in wastewater treatment.

#### **1.4** The novelty of the Study

The natural clay sample collected from the clay deposits in northern BC was characterized by the author to know its different constituents and properties, which was completely unknown before. Furthermore, to the best of the author's knowledge, the modification method used in this project has never been used to modify natural clay consist of kaolinite and illite for removing phosphorus from water. Besides, the statistical method used to optimize the process parameter and develop the model for the prediction of the phosphorus adsorption performance of the natural and zirconium-modified clay will be an important addition in the field of phosphate/phosphorous removal study from wastewater.

# **2** Materials and Methods

#### 2.1 Materials

Natural clay samples had been collected from Northern British Columbia (BC) deposits provided by Mindbody Networks Inc. The gravel and debris in the raw samples were separated by hand and then dried in an oven at 105°C for 24 hours. Then the dried samples were hand ground by mortar and pestle, sieved to 0.053 mm (ASTM-E11), and packed in a plastic zipper packet for further use. All the chemicals used in this study including, ZrCl<sub>4</sub> (Merck), NaH<sub>2</sub>PO<sub>4</sub> (Life Science), NaOH (Fisher Scientific), and HCl (34-37%, BDH Chemicals), were in reagent grade.

### 2.2 Preparation of Zirconium modified clay

Zirconium-modified clay was prepared following a previous study with few modifications (Lin et al., 2019). The clay was modified with Zirconium salt by dissolving five grams of ZrCl<sub>4</sub> salt in 100 mL deionized water and then adding 10 g of the natural clay sample to the solution. The suspension was then magnetically stirred for 1.5 hours. After that, a 1 mol/L NaOH solution was slowly added dropwise to the suspension. The suspension was kept under magnetic stirring during

the addition of the NaOH solution until the pH of the solution reached 10. The suspensions were then magnetically agitated for 1 more hour. Then, the Zr modified clay was separated by centrifugation, followed by repeated washing with deionized water, and drying in a 105°C oven for 24 hours. Finally, the obtained dry material was stored for further use.

## 2.3 Preparation of Granulated Natural and Zr modified clay

Shaping and forming steps were performed to make granular shaped adsorbent from fine powder form by using a modified method from previous studies (Siwek et al., 2019, Charkhi et al., 2012) to use them in continuous column experiment to maintain the pressure drop of the column. First, Sodium alginate (SA) solution (2%, w/v) was prepared using distilled water under constant stirring at room temperature until it turned into a homogenous mixture. Then, 10 g of each clay was placed individually in SA solutions and agitated for two hours to achieve uniform dispersion. After that, the polymer solutions containing SA/clay and SA/ZrMC were inserted into a 10 -mL syringe and then extruded into a cross-linking solution containing calcium chloride (0.155 M) with constant stirring. The granules were produced instantly but kept there for an additional hour for a complete cross-linking reaction. Then the granules were washed with distilled water and then kept at room temperature for 24 hours. Then for the final drying step, the granules were kept at 600 °C for 24 h in an electric furnace using a controlled heating program with a heating rate of 6°C/min to decompose the alginate content of the granules.



Fig. 1: (A) Clay-alginate beads formed in CaCl<sub>2</sub> Solution; (B) Clay granules after washing and drying at room temperature for 24 h; (C) Clay granules before calcination and (D) after calcination at 600°C for 24 h.

# 2.4 Characterization of Natural and modified clay

Different physiochemical properties of the natural and modified samples were determined. The crystalline structure of the adsorbents was characterized using X-ray diffraction (parameters: CuK $\alpha$  [ $\lambda$ =1.54059Å], 3°<20<90° with a step width of 0.02°, 40kV, 15mA) (Rigaku Miniflex 600 6G). To determine the amount of zirconium attached to the clay and the risk of entering heavy metals contamination, the XRF analysis (Rigaku, NEX-QC+EDXRF) was employed to determine

the chemical composition of the samples. To determine the elemental composition of the adsorbents, the adsorbents (in 3 replicates) were digested using the reverse aqua regia method (Modified version of EPA 3050B method) (USEPA 1996) and analyzed by ICP-OES (Agilent SVDV 5100 ICP-OES). The surface morphology of samples was obtained by scanning electron microscope (SEM, PHILIPS XL 30) operating at 10 keV of acceleration voltage. ATR-FTIR technique (Platinum ATR Alpha II FTIR Spectrometer, Bruker) was used to identify the IR spectra of adsorbents. Thermogravimetric Analysis (TGA) was performed on the clay samples by Discovery TGA (TA Instruments 954000.901) and Brunaur-Emmett-Teller (BET) specific surface areas, and the pore distribution of samples was measured using Autosorb-1 device (Quantachrome instrument) at 77K.

# 2.5 Adsorption Batch Experiment

Orthophosphate was the form of phosphorus used in this study. Phosphorus in wastewater exists in many different forms. The common forms are orthophosphate, polyphosphates, and organicallybound phosphates (Bacelo et al., 2020). These different forms tend to end up as orthophosphate. Polyphosphates which are condensed orthophosphates, hydrolyze in water to produce soluble orthophosphate, while the bacterial decomposition of organically bound phosphate also produces orthophosphate. Orthophosphate is the predominant phosphorus species found in wastewater (Naimpally and Rosselot, 2013, Masters and Ela, 2008); hence orthophosphate was chosen as the phosphorus species, and an aqueous solution of Na<sub>2</sub>HPO<sub>4</sub> was used as the artificial wastewater for this study.

# 2.5.1 Preliminary Phosphorus Adsorption Tests

In a preliminary set of experiments, the adsorption-desorption tests (in two replicates) were performed on natural clay, and Zr modified clay. To load the phosphorous up to clay sorption capacities, 0.5 g of each sample was transferred to a 50-mL conical polyethylene tube, and 20 mL of 100 mg/L P solution was added. The mixture was agitated for 24 hours at room temperature using a rotary shaker. After that, samples were centrifuged and the concentration of P of the solution was determined using ICP-OES. In addition, the concentration of other metals present in the solution was analyzed with ICP-OES to investigate if the adsorbents had leached any of those metals into the solution during adsorption. The precipitate ("P" loaded sample) was washed with deionized water twice to remove the loosely held and unabsorbed P from the sample. Then, to get rid of the water, the samples were dried at 105 °C for 24 hours in an electric oven. To study the P desorption, 0.1 g of "P" loaded sample was transferred to another 50-mL centrifuge tube and 20 mL deionized water was added and the mixture was agitated for 24 hours at room temperature  $(25^{\circ}C)$ . After centrifuging the mixture, the concentration of P in the supernatant was determined. All P solutions were made using a P stock solution (1000 mg P/L) which was prepared by dissolving the proper amount of Na<sub>2</sub>HPO<sub>4</sub> salt in deionized water and pH was adjusted on 7.0 using 0.1 M NaOH or HCl. To assess the P sorption behaviour on the clay samples, different parameters such as contact time, adsorbent dosage, pH, and initial concentration was studied by designing different batch adsorption tests where each test was run in three replicates.

# 2.5.2 Effect of Contact Time

To evaluate adsorption kinetics, a set of experiments were conducted by varying contact times of 15, 30 min, 1, 2, 4, 8, 16, 24 h. Since the adsorption capacity of NC was much lower than ZrMC, different doses were used. For NC, 0.5 g was weighed and transferred to a 50-mL centrifuge tube and 20 mL of 5 mg/L P solution was added. For the ZrMC, by using a microbalance, 20 mg of ZrMC was weighed and transferred to a 50-mL centrifuge tube and 20 mL of 5 mg/L P solution

was added. Then the supernatants were collected after centrifuging the mixtures at 4000 rpm for 10 min and kept for further analysis to determine the P concentration by ICP-OES.

## 2.5.3 Effect of pH

pH is one of the most important factors affecting the adsorption processes. To study the effect of pH, the different solutions, with pH ranging 2-9 by using dilute NaOH and HCl and containing 10 mg/L of 20 mL P solution was prepared and added to 50 mL plastic propylene tubes containing 0.5g and 0.02 g of natural Zr modified adsorbents, respectively. Then the solutions were shaken at room temperature for 24 h and centrifuged at 4000 rpm for 10 min to separate the supernatants, which were later analyzed in ICP-OES for P concentration measurement.

# 2.5.4 Determination of point of Zero Charge (pHpzc)

The point of zero charges (pHpzc) of NC and ZrMC before and after adsorption were determined using the pH drift method (Rivera-Utrilla et al., 2001). The pH drift method, which provides a fast but reliable method for the determination of pHpzc was originally developed for activated carbon has been used for the determination of pHpzc in clay (Moharami and Jalali, 2013). The method has been compared to the standard method of zeta potentiometric titration and mass titration with similar results.

20 mL of 0.01M NaCl was placed into 50 mL Erlenmeyer flask. The pH of each flask was adjusted to 2, 3, 4, 5, 6, 7, 8, 10, and 12 by adding the appropriate amount of 0.1M HCl or 0.1M NaOH solution. 0.06g of the adsorbents was added to each flask and left undisturbed for 48 hours. The final pH was measured after 48 hours. A graph of final pH was plotted against the initial pH and the pHpzc was the point where the line of the final pH versus initial pH crossed the line equal to final pH.

#### 2.5.5 Effect of Adsorbent Dosage

To study the effect of adsorbent dosage for NC 0.25, 0.5, 1, 1.5, 2 g of samples were weighed and transferred to 50-mL centrifuge tubes and 20 mL of 10 mg 'P'/L solution was added. For the ZrMC, 20, 50, 100, 150, and 200 mg of sample was weighed, transferred to the 50-mL centrifuge tubes and 20 mL of 50 mg 'P'/L solution was added. The mixtures were shaken for 24 h using a rotary shaker at room temperature. In the end, the mixtures were centrifuged, and the concentration of P was determined by ICP-OES in the filtrate.

#### 2.5.6 Effect of Initial Phosphorus Concentration

The effect of different initial phosphorus concentrations was studied by contacting 20 mL of P solutions with different concentrations, 1, 2, 5, 10, 15, 20, 30 and 50 mg/L, with 0.5 g of NC and 0.02g of ZrMC for 24 hours in a rotating shaker at room temperature. Then, they were centrifuged at 4000 rpm for 10 min and the P concentrations in the supernatants were measured by ICP-OES. In the case of ZrMC, a lower adsorbent dose was used due to the higher adsorption capacity of the sample than NC.

# 2.5.7 The effect of matrix interferences (the effect of co-ions and soluble organic compounds)

To evaluate the adsorption performance of the adsorbent for P removal from actual wastewater, a sample from the Prince George city wastewater treatment plant with a total-P concentration of 1.2 mg/L was used. The sample collected from the waste lagoon was characterized using ICP-OES and IC to determine the chemical composition of the sample (the results are mentioned in Table A1). In the trials, NC and ZrMC were weighed 0.15g and 0.015g, respectively to 50-mL centrifuge tubes. A volume of the wastewater (0, 15, 25, or 40 mL) was then added to each tube and diluted to a 50mL graduation mark with deionized water. To further observe potential effects of

competitive interference on P adsorption, a replicate of one of the trial dilutions was subjected to varied additions of arsenic to provide an initial total arsenic concentration of 0, 0.30, 2.55, and 5.108 mg/L. The tubes were then placed on a rocking table platform shaker at 100 rpm for 24h. Then the mixtures were kept settling for 2 days and after the settling period, the supernatants were extracted to determine the extent of total-P removed following treatment via ICP-OES.

# 2.6 Kinetic and Isotherm Experiment

#### 2.6.1 Kinetic Experiment

Several steps can be used to examine the controlling mechanism of the adsorption process such as chemical reaction, diffusion control and mass transfer. Kinetic models are used to test experimental data from the adsorption. The kinetics of adsorption onto NC and ZrMC is required for selecting optimum operating conditions for the full-scale batch process. The kinetic parameters, which are helpful for the prediction of adsorption rate, give important information for designing and modelling the adsorption processes. Thus, the rate of adsorption was determined from the amount of phosphorus adsorbed at different times and the adsorption data from Section 2.5.2 was used to evaluate for pseudo-first order, pseudo-second order and intra-particle diffusion kinetics models to determine which model best suits the adsorption. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients ( $\mathbb{R}^2$ ). The relatively higher  $\mathbb{R}^2$  value ( $\approx$ 1) is the more applicable model to the kinetics of adsorption. The linear form of pseudo-first order and pseudo-second order models can be written as equations 5 and 6 (Guo and Wang, 2019):

$$Pseudo - first order: ln(q_t - q_e) = lnq_e - k_1 t$$
(5)

Pseudo – second order:  $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$  (6)

Where t is the time (hr),  $k_1$  and  $k_2$  are related to the adsorption rate constant (hr<sup>-1</sup>, g/mg hr),  $q_t$  and  $q_e$  are the sorption capacity at t and equilibrium (mg/g).

To investigate the multiple steps in the adsorption including the diffusion of adsorbate from the solution phase into the surfaces and subsequently to the pores of the adsorbent, the intraparticle model, provides mechanistic information (Morris and Weber, 1962). The pore diffusion process is typically slow and thus determining the rate of adsorption.

Intra – particle diffusion: 
$$q_t = k_p t^{1/2} + C$$
 (7)

Where  $q_t$  is the amount of phosphorous adsorbed per mass of the adsorbent (mg/g) at time t, C is related to the thickness of the boundary layer, and  $k_p$  is the intra-particle diffusion rate constant (mg/g min<sup>1/2</sup>).

# 2.6.2 Adsorption Isotherm

At constant temperature, the relation between the amount adsorbed on the solid and the concentration in the fluid is called an isotherm. To present a better understanding of phosphorous on the different adsorbents, two common isotherm models were used to simulate the adsorption experiments. The nonlinear form of the isotherm models can be written as below (Foo and Hameed, 2010):

The Freundlich model

$$q_e = K_f C_e^n \tag{8}$$

The Langmuir model

$$q_e = \frac{K_L Q C_e}{1 + K_L C_e} \tag{9}$$

where  $q_e$  (mg/g) and  $C_e$  (mg/l) are the sorption capacity and sorbate concentration at equilibrium;  $K_f$  (mg/g)(L/mg)<sup>n</sup> and  $K_L$  (l/g) are Freundlich and Langmuir's constants related to the affinity and; n is the Freundlich constant, representing the sorption intensity and Q (mg/g) is the monolayer sorption capacity (the maximum adsorption capacity predicted by Langmuir model). The results of the experiment described in Section 2.5.6 were used in the study of the adsorption isotherm. The equilibrium adsorption capacity was derived from the isotherm data and Langmuir and Freundlich isotherm models were used to analyze the relationship between the quantities of phosphorus adsorbed onto the clays.

## 2.7 Optimization Using DOE and RSM Statistical Methods

In this study, a full factorial design of experiment (DOE) was developed using Minitab software (version 18, Minitab, Inc., USA) to examine the effects of four independent variables on phosphorus removal by natural and modified clay. These four variables were adsorbent dose, initial concentration, pH, and contact time. DOE is a method for analyzing any response that varies in response to one or more independent factors. Two-level full factorial DOE is a special subset of general factorial designs as it has only two levels of each variable. These experiments are designated for 2<sup>k</sup> runs, where k is the number of variables and 2<sup>k</sup> represents the number of unique runs in each replicate of the design. The 2<sup>k</sup> experiments can describe all of the variables under investigation as well as resolve two-factor and higher-order interactions when all of the runs are done in random order. (Mathews, 2005). Using Minitab software, in this work, a 2<sup>4</sup> complete factorial design of experiment (DOE) was developed to investigate the effects of four independent factors on P removal by NC and ZrMC. The independent variables of experimental conditions were applied as indicated in Table 1 based on preliminary test findings. For each type of adsorbent, the number of total runs was 54, including 3 replicates and center points. The parameters involved

in these experiments were then analyzed by using response surface methodology (RSM) on Minitab software.

RSM is a set of mathematical and statistical methods used to optimize chemical reactions and industrial processes (Dong and Sartaj, 2016) The quadratic equation below usually describes the behaviour of the system (Burdick et al., 2005)

$$Y_{1} = f(x) = A_{0} + \sum_{i=1}^{n} A_{i}X_{i} + \sum_{i=1}^{n} A_{ii}X_{i}^{2} + \sum_{i\neq 1}^{n} A_{ij}X_{i}X_{j} + \varepsilon$$
(10)

where  $Y_1$  is the outcome response,  $X_i$  and  $X_j$  are the independent variables,  $A_0$  is the value of the fixed response at the center point of the design,  $A_i$ ,  $A_{ii}$  and  $A_{ij}$  are the interaction coefficients of linear, quadratic and second-order terms, respectively, n is the number of independent variables, and  $\varepsilon$  is the random error. The accuracy of the model was evaluated by the correlation coefficient ( $R^2$ ) (Burdick et al., 2005). In this study, RSM was used for evaluating the process of P removal from solution through optimizing %P removal as the response.

Independent Variable	Factor	Coded Levels					
		NC			ZrMC		
		-1	0	+1	-1	0	+1
Initial Concentration (mg/L)	А	5	17.5	30	5	17.5	30
Adsorbent dose (g/L)	В	10	25	50	0.2	0.4	1
Contact time (hour)	С	1	8	16	1	8	16
pH	D	5	7	9	5	7	9

Table 1: Independent variables of the experimental design

To perform the DOE, different concentrations of P solution were prepared by dissolving a known amount of Na<sub>2</sub>HPO<sub>4</sub> salt in deionized water and the pH of the solutions was adjusted by 0.1 mol/L NaOH or HCl solution to the desired values. Then desired amounts of adsorbents were mixed with the desired concentration of 20 mL P solution in 50 mL plastic vials. The plastic vials were shaken by a rotating shaker at 100 rpm at room temperature for the targeted contact time. Then, the plastic vials were centrifuged at 4000 rpm for 10 min to settle fine clay particles and the supernatant solutions were collected for further analysis. The spent adsorbents were washed with DI water once and dried at 105°C in an oven overnight. The filtered solutions were analyzed by ICP-OES to determine the P concentrations. The measured amounts of P were used to calculate the percent P removal efficiency.

# 2.8 Fixed Bed Column Experiment

For the continuous removal of phosphorous, a fixed-bed column experiment was designed (100 mm in length and 10 mm in internal diameter) using a glass burette with a 500 mL reservoir on top of it. Then the column was loaded with the granulated NC and ZrMC separately. A synthetic feeding solution (5.35 mg/L of P) was fed as a downward system, and by using a peristaltic pump, the speed of flow rate was adjusted to 10.0 mL/min (Figure 2). In the first 20 minutes, 10 mL of the output solution was collected every minute to investigate the concentration profile at the start during this time. After 20 minutes, each 10 mL solution was collected every 10 minutes. All the collected output solution was analyzed for total P by ICP-OES. The breakthrough concentration (maximum allowable concentration in the effluent) was considered to be 0.5 mg/L (Shi et al., 2019, Wang et al., 2020). After the column experiments, the adsorbents were dried in the oven at 105°C temperature for 24 hrs and ground to a fine power and stored for further analysis. The Yoon-Nelson

model was employed to describe the column adsorption capacity and different parameters were calculated (Lalley et al., 2016).

$$\ln\left(\frac{c_t}{c_t - c_i}\right) = K_{YN}(t - \tau) \tag{11}$$

where  $C_t$  and  $C_i$  are the P concentrations (mg/l) at the time (t) in the effluent and the influent, respectively, t is the column service time or residence time (min),  $\tau$  is the time required for 50% adsorbate breakthrough (min), and  $K_{YN}$  is the proportionality constant (min<sup>-1</sup>).



Fig. 2: A column designed for the adsorption study with NC and ZrMC in a continuous system.

# **3** Results and Discussion

# 3.1 Adsorbents Characterization

The chemical composition of the samples (two replicates) was analyzed by XRF and the results have been mentioned in Table A2. From Table A2, the result showed high silica, aluminum, iron and calcium content. The high  $K_2O$  (3.52%) content in the natural clay samples is probably due to the relatively large amount of illite content (Sultana et al., 2015). In the case of ZrMC, the zirconium content is higher than NC, which confirms that the modification process was successful.

No significant difference was observed between the natural and modified clay samples' XRD pattern (Fig A1), which indicates that the modification process did not have any effect on the crystallinity framework of the clay samples because of the presence of the amorphous nature of the precipitated zirconium hydroxides. Furthermore, the analysis of the XRD patterns indicated that clay samples consist mainly of quartz, illite, kaolinite, nontronite, and calcium carbonates in their dominant mineral phases.

TGA curves (Fig A2) of the adsorbents show the weight percentage loss of the samples with increasing the temperature at a heating rate of 10°C/min. The TGA curve for the natural clay sample showed a total of 9.8% of weight loss, consisting mainly of three phases- the first (around 1% loss) starts at around 42°C and ends at 92°C, corresponding to the departure of the water adsorbed by the clay. Another major change occurred starting at around 430°C to 520°C, where the sample lost 3.19% weight due to the decomposition of kaolinite (Wang et al., 2011). The third change begins at 654°C and ends at around 710°C losing about 3.80% of its total weight due to the decomposition of carbonates (Elgamouz and Tijani, 2018). In the case of ZrMC, the total weight loss was 5.4% higher than in NC, because of the decomposition of zirconium oxides and hydroxides present in the modified sample (Al-Hazmi et al., 2014).

The BET analysis of the natural and modified samples (Table A6) indicates that after the modification increased the surface area of the sample increased from 26.88 m<sup>2</sup>/g to 109.92 m<sup>2</sup>/g. On the other hand, the average pore diameter decreased in the modified sample from 10.08 to 4.73 A°. However, the volume of micro pores increased in ZrMC significantly, from 0.070 to 0.130 cm<sup>3</sup>/g. Overall, the results from the BET analyzer indicate a higher adsorption capacity of the modified sample.

The SEM study of the clays revealed particles with pseudospherical shape and when examined closely, these shapes appeared as sheet aggregates, sometimes indistinguishable from one another. (Fig A3). Similar micrographs were observed for different clay materials in literature (Ogunmodede et al., 2015, Muhmed and Wanatowski, 2013). In the case of ZrMC (Fig A4), the surface morphology appeared to possess more irregular textures and porous cavities, which can be considered as available sites for adsorption.

From the trace elemental analysis results (averaged from 3 replicates) (Table A3) obtained from ICP-OES of the adsorbents after acid digestion, it was observed that the Zr amount is significantly high in the modified sample which confirms the effectiveness of the modification process. In addition, the results showed that the samples did not contain a significant amount of trace elements according to the values of the Canadian Environmental Quality Guideline (Table A4), which could affect the environment (CCME, 2007). Furthermore, the leachate analysis of the adsorbents (Table A5) confirms that the adsorbents do not release any heavy metal in the solution during the adsorption process. It was also observed that the zirconium concentration is very low in the solution, which indicates the modified sample did not release any free zirconium in the water and thus, proves the successful attachment of the zirconium during the modification process.

## 3.2 Batch Adsorption Test

# 3.2.1 Preliminary Adsorption-Desorption Test

Fig 3 shows the adsorption capacity and desorption behaviour of natural and modified clay samples. The results revealed that the adsorption capacity of the clay increased by more than five times higher than the natural clay after Zr modification. Additionally, the desorption rate also decreased after modification. For natural clay, 21.4% of the total adsorbed P was desorbed in the DI water after the desorption test, while the percentage was only 0.1% with Zr modified clay. Thus, it was observed that the modification process was successful in enhancing the adsorption performance of the clay.



Fig. 3: Preliminary adsorption-desorption test with NC and ZRMC (initial P conc=100 mg/L; pH=7; Contact time=24 hrs; adsorbent dose= 0.5 g;) Error bars represent standard deviation

(n=2).

# 3.2.2 Effect of Contact Time

The results of the kinetic experiment are presented in Fig 4. The adsorption speed could be divided into two stages in all cases. In the first stage, the adsorption takes place rapidly during the first 30

min where the kinetic profile shows a steeper gradient. At the end of this stage, total P removal was attained as 71.2%, and 62.1% for the NC and ZrMC, respectively. The following stage was relatively slow and started after that and continued up to 16 hours. After this stage, 84.8 and 91.2% of initial phosphorous were removed by NC and ZrMC, respectively. After that, no significant increase was observed for the absorbents. The initial rapid absorption is most likely owing to a large number of accessible vacant adsorption sites; as phosphorous is removed from the solution, the number of these sites decreases, and the slope becomes more gradual as the rate of adsorption decreases (Lin et al., 2019). When the reaction approaches equilibrium, or all of the phosphorus has been removed from the solution, the rate of reaction slows down.





Fig. 4: Sorption kinetics of P by the NC and ZrMC (initial P conc= 5 ppm; pH=7; NC dose= 0.5gm/ 20mL solution, ZrMC dose= 0.02g/ 20 mL solution). Error bars represent standard deviation (n=3)

# 3.2.3 Effect of pH

The effect of pH, in the range 2 to 9on P adsorption by different adsorbents has shown in Fig 5. It was observed that the adsorption capacity of both clays decreased by increasing the pH. The adsorption capacity for NC and ZrMC at pH 2 was 0.193 and 8.99 mg/g, while at pH 9 was 0.186 and 5.95 mg/g, respectively. At lower pH, some of the clay surfaces carry a more positive charge and thus attracting more negatively charged phosphate ions in solution (Chitrakar et al., 2006). As the pH increases, the surface of the clay becomes more negatively charged by deprotonation of – OH groups, resulting in the increased repulsion between the negatively charged phosphate ions and the clay surface (Xue et al., 2009). Additionally, by increasing the pH, the competition of OH-with phosphate species also increases. As a result, a decrease in P adsorption is observed by increasing the pH of the solution. The decrease of phosphorus adsorption capacity with the increase

of initial pH also was found in previous studies of different clay materials (Moharami and Jalali, 2015, Huang et al., 2008).

Compared to NC, the adsorption of P by ZrMC is more affected by pH. This is similar to many reports using other Zr-containing adsorbents (Zhang et al., 2013, Huang et al., 2015). In acidic conditions, the protonation of surface functional groups and Zr release from the surface of clay increases the adsorption (Kumararaja et al., 2019).





Fig 5: The effect of pH on P adsorption by the NC and ZrMC (NC dose= 0.5 g/20 mg P Solution, ZrMC= 0.02 g/mL; Contact time= 24h; Initial conc=10 mg P/L). Error bars represent standard deviation (n=3).

# 3.2.4 The effect of adsorbent dosage

The impact of adsorbent dose on P removal by various adsorbents is shown in Fig 6. In all cases, increasing the dose, the removal efficiency of P increased, but the adsorption capacity declined. For NC, the adsorption removal efficiency increased up to the third adsorbent dosage (50g/L), and then it reached an equilibrium condition. While for the ZrMC, a sharp increase in removal efficiency was observed with increasing adsorbent dose up to 8g/L and after that increasing from 8 to 10g/L it did not show significant P uptake. By increasing the dosage, the active sites for P adsorption increased and it caused to remove more P from the solution. This result is consistent with results reported in various studies. Jia et al. (2013) reported an increase in the removal of phosphate as the dosage of used bricks (obtained from housing projects) increased from 5 to 30 g/L (Jia et al., 2013). Pawar et al. (2016) also reported an increase in the removal of phosphate as
the dosage of aluminum-pillared acid-activated bentonite beads and alginate aluminum-pillared acid-activated bentonite beads increased from 1 to 5 g/L (Pawar et al., 2016).



Fig. 6: The effect of adsorbent dosage on P adsorption by the NC and ZrMC (Contact time=24 hr; pH=7; Initial conc for NC= 10 mg/L, for ZrMC= 50 mg/L). Error bars represent standard deviation (n=3).

#### **3.2.5** Effect of Initial P Concentration

The effect of the initial concentration on the adsorption of phosphorus was studied on various concentrations of phosphorus ranging from 5 to 50 mg/L and the result is presented in Fig 7. For both adsorbents, the adsorption capacity increased and removal efficiency decreased by increasing the initial concentration. At lower concentrations, the ratio of available active sites to the amount of phosphate ions present in the solution is high and with excess adsorption sites, the adsorption saturation could not be reached (Rout et al., 2014). As initial P concentration increased, the ratio of adsorbent to phosphate ions present in solution decreased and active sites were more difficult to find due to the fixed number of available sites for any given mass of absorbent (Das et al., 2006). This resulted in greater competition between phosphate ions present in solution for the available active sites resulting in decreased removal efficiency as the concentration increased. These results are similar to the results obtained by Rout et al. (2014). On the other side, increasing initial concentration, the number of phosphate ions available for binding onto the active sorption sites of the adsorbents surface also increase. This increase in the amount of phosphate ions led to a higher rate of collision between the phosphate ions and the adsorbent's surface which also increased the driving force required to lower the mass transfer resistance between the clay and the phosphate solution (Dawodu and Akpomie, 2014). Thus, an increase in adsorption capacity was observed due to increasing the initial P concentration.



Fig. 7: Sorption isotherm of P by the NC, and ZrMC (NC Dose= 0.5g/20mL solution, ZrMC= 0.02g/20mL; Contact time=24 hr; pH=7). Error bars represent standard deviation (n=3).

## 3.2.6 Adsorption Isotherm Study

To present a better understanding of phosphorous on the different adsorbents, two common isotherm models, the Langmuir and the Freundlich were used to simulating the adsorption experiments. The data from Section 2.5.6 was used for the analysis of the adsorption isotherm. The isotherms were analyzed using theories discussed in Section 2.6.2. The isotherm models have been fitted to the experimental data and the parameters are calculated and presented in table 2. Regarding the  $R^2$  and standard errors of the estimate, SEE, the Langmuir model has better fitted to experimental data (higher  $R^2$  and lower SEE). The Langmuir isotherm assumes adsorption takes place at specific energetic homogeneous sites forming a monolayer surface coverage without any interaction between sorbed molecules (Wibowo et al., 2017). Based on the calculated parameters, the ZrMC was more efficient than NC for P removal, as the maximum adsorption capacity, Q<sub>max</sub> and  $K_L$  for ZrMC was 11.834 mg/g and 1.849 l/g and for NC,  $Q_{max}$  and  $K_L$  was found 0.493 mg/g and 0.695 l/g respectively. Additionally, in the case of the Freundlich isotherm model, the 'n' value indicates the degree of nonlinearity between solution concentration and adsorption whereas, the value below 1 implies a chemisorption process and above 1 indicates a physical process (Foo and Hameed, 2010). The values of n within the range of 1–10 represent good adsorption and since in the present study, n lies between this range, it indicates that a physical adsorption process occurred between P onto the adsorbents with high adsorption intensity (Hameed et al., 2007).

Table 2: Langmuir and Freundlich isotherm parameters of phosphorous adsorption onto NC, and<br/>ZrMC.

	Freundlich model				Langmuir model			
	п	$K_f(mg/g)(L/mg)^n$	$R^2$	SEE	$Q_{max}(mg/g)$	$K_L(l/g)$	$R^2$	SEE
NC	3.007	0.176	0.914	0.075	0.493	0.695	0.998	0.059
ZrMC	3.173	5.009	0.745	0.136	11.834	1.849	0.998	0.046



Fig 8: The adsorption isotherm plots for the adsorption by NC and ZrMC: a) Langmuir adsorption isotherm; b) Freundlich adsorption isotherm

## 3.2.7 Adsorption Kinetics Modelling

Several kinetic models, namely pseudo-first order, pseudo-second order, and intraparticle diffusion models were used to determine the rate order and adsorption mechanism for natural and modified clay. The different models were fitted to kinetic data and the parameters presented in

Tables 3 and 4. The kinetic data fitted the pseudo-second order model well, indicating that chemisorption may be dominant in P sorption by the adsorbents. This conclusion is based on the fact that the pseudo-second-order kinetic model assumes the rate-limiting step might be chemical adsorption, which includes exchanged or shared electrons between absorbent and adsorbate (Azizian, 2004). Additionally, the pseudo-second order model assumes a monolayer adsorption mechanism which agrees with the Langmuir isotherm model (Lalley et al., 2016).



Fig. 9: The Pseudo-first order kinetic model fitting on the NC, and ZrMC adsorption data



Fig. 10: The Pseudo-second order kinetic model fitting on the NC, and ZrMC adsorption data

 Table 3: Pseudo-first and pseudo-second order kinetic parameters of phosphorous adsorption onto NC, and ZrMC.

	Pseudo-first order				Ps	Pseudo-second order			
	$k_1(1/h)$	q <sub>e</sub> (mg/g)	$R^2$	SEE	$k_2(g/mg h)$	qe(mg/g)	$R^2$	SEE	
NC	0.184	0.032	0.772	0.627	0.034	0.170	0.999	0.518	
ZrMC	0.227	1.655	0.986	0.172	0.013	4.684	0.999	0.038	



Fig. 11: The two-site intraparticle diffusion kinetic model fitting on (A) NC, and (B) ZrMC adsorption data.

The consistency of experimental data with intraparticle diffusion could confirm the results of pseudo-second order model because either intraparticle diffusion or chemisorption is a ratecontrolling step. The intraparticle diffusion model explains the movement of phosphate ions through adsorbent channels, cages, and pores, whereas the chemisorption mechanism is the consequence of ion exchange interactions between adsorbent surface functional groups and P species (Velazquez-Peña et al., 2019). The amount of  $k_p$  for the second phase is lower than its amount for the first phase, confirming the slower rate of reactions in the second phase.

Table 4: Intraparticle diffusion parameters of phosphorous adsorption onto NC, and ZrMC.

	First phase				Second phase				
	$k_p(mg/g min^{1/2})$	С	$R^2$	SEE	$k_p(mg/g min^{1/2})$	С	$R^2$	SEE	
NC	0.1473	0.0003	0.904	0.020	0.0037	0.0024	0.682	0.002	
ZrMC	2.837	0.843	0.945	0.064	0.2515	1.253	0.864	0.164	

#### 3.2.8 Influence of matrix interferences

A set of experiments were performed using synthetic wastewater with phosphorous, real wastewater with phosphorus and/or arsenic and the results were analyzed to check the matrix interferences (the effect of co-ions and soluble organic compounds) in P adsorption by the adsorbents. Figure 12C shows the removal efficiency of total-P relative to the equilibrated solution concentration tested. The amount of total-P removal from lagoon wastewater across the prescribed loading regimes is shown in Figures 12A and 12B about the mass of each adsorbent, where the profiles maintain linearity and the slopes correspond to a percent removal efficiency ZrMC had greater efficiency at removing total-P than NC at much higher loading ratios.

With matrix interference involvement, the adsorption capacity decreased by 16.5% and 14.7% with ZrMC and NC, respectively comparing to the results of the adsorption experiment without the matrix interference. The reason behind this could be explained as an effect of pH, matrix and co-ion interferences. As shown in Table A1, the pH of lagoon wastewater was 8.02 and contained some anions.

The decrease in total-P removal efficiency for a set of duplicates treated to arsenic ion interference is shown in Figure 12D. Each of these treatments started with 1mg/L total-P derived from the wastewater. The intercept represents the degree of adsorption without arsenic interference, whereas the slope reveals the type of arsenic interference in terms of competitivity or cooperativity. In Figure 12D, the negative slope indicates a decrease in efficiency with increasing total As concentration. As can be seen, the arsenic showed a higher effect in P adsorption on ZrMC, because of having a higher slope absolute value (0.894) than NC (0.101). However, because the ratio of arsenic to adsorbent was greater for ZrMC, the relative impact of total-P removal depending on the slope could not be directly compared. A similar kind of arsenic/phosphorous competitive behaviour has been reported in several previous studies (Moraga et al., 2019, Awual et al., 2011, Carabante et al., 2010).





Fig 12: The effect of matrix interference: the relation between available P in lagoon wastewater and removed P by each g of (A) ZrMC; (B) NC; (C) the effect of initial P conc. in lagoon wastewater on P adsorption capacity of ZrMC and NC; (D) the effect of arsenic initial conc. on adsorption capacity of the clays in real and synthetic wastewater on P adsorption by NC (dose= 3g/L), and ZrMC (dose= 0.3 g/L).

#### 3.2.9 Phosphorus Adsorption performance of Granulated NC and ZrMC

The phosphorus adsorption capacity of the granulated clay adsorbents was evaluated, and the results are shown in Fig 13. For both adsorbents, the adsorption capacity decreased after granule formation but after the calcination at 600°C for 24h, the adsorption capacity of the adsorbents increased and reached a value, higher than the powder form for both natural and modified samples. During the granule formation, alginate compounds are trapped in the pores of the adsorbents, which lowers the adsorption capacity, but after the calcination at high temperature, all the alginate content and some other organic impurities are decomposed (Charkhi et al., 2012), which increases the free pore space in the final products and thus shows a higher adsorption capacity than the powdered adsorbents.



Fig 13: P removal performance by powdered and granulated (A) natural clay; (B) Zr modified clay; (before and after calcination) (Initial P conc= 11.45 mg/L; Contact time= 24 h; pH=7; all NC dose=0.5 g/ 20 mL solution, all ZrMC dose= 0.03 g/20 mL solution). Error bars represents standard deviation (n=2)

#### 3.3 Optimization Study Using DOE and RSM Statistical Methods

After performing 54 sets of experiments for each type of clay, based on a full factorial design of four independent variables (initial conc, pH, time, and adsorbent dosage), the experimental results for P removal efficiency (%)ranged from 2.1 to 91.6%, and 31.2%- 99.9% for NC and ZrMC respectively. The multi-variable regression model for the response P removal percentage was established and the efficiency of the operating variables was assessed by the percent contribution and Pareto analysis. Insignificant terms were eliminated from the model and a reduced model was established. The R<sup>2</sup> value of the established model was checked to determine the significance of the model. The reduced model was also used to optimize the conditions to maximize the percent removal for each clay sample as well as to predict the percent removal efficiency for all the conditions applied to DOE.

### 3.3.1 Optimization results for Natural clay

The multi-variable regression model for the response P removal percentage was predicted by the following equation shown as Eq. (12) below:

% P Removal = 
$$130.03 - 6.84 \text{ A} + 29.92 \text{ C} - 1.75 \text{ D} - 6.26 \text{ AC} + 0.416 \text{ AD} + 1.63 \text{ CD} - 0.377$$
  
ACD (12)

Where, A=Initial P Conc in mg/L (5-30); B= adsorbent dose in g/L (10-50); C= Contact time in hour (1-16); D= pH (5-9)

Equation 12 indicates the effects of each independent operating parameter and their two-way, three-way, and four-way interactions to remove phosphorus from aqueous solution by the natural clay adsorbent. The correlation coefficient ( $R^2$ ) for the model, was 98.28%. The accuracy of the model was checked by the analysis of variance (ANOVA) and Pareto chart (Fig. 14). To evaluate

the statistical significance of the developed model, the F test was performed for the analysis of variance (ANOVA) by determining the F statistic value and the P value. P value is a probability that measures the evidence against the null hypothesis. The higher F value with the combination of the lower P value (Table A7) indicates that the results are significant (Miller Jr, 1997).

The fitness of the model was evaluated by the value of the coefficient of determination ( $\mathbb{R}^2$ ), adjusted  $\mathbb{R}^2$  and predicted  $\mathbb{R}^2$ . The predicted  $\mathbb{R}^2$  indicates the performance of a regression model to predict responses for new observations (Myers et al., 2016). The  $\mathbb{R}^2$  value of 0.993 indicates that the predicted values obtained from the model are a very good fit for the experimental data.  $\mathbb{R}^2$  adjusted value of 0.992 indicates that 99.2% of the total variation in phosphorus adsorption data can be described by the selected model. In the reduced model, the P-value (Table A7) for lack-of-fit is 0.450, which is greater than 0.05, indicating that the lack-of-fit is insignificant relative to the pure error (Ding and Sartaj, 2015).

Fig 15 illustrates the predicted versus experimental (actual) values for %P removal. The R<sup>2</sup> value of 0.995 indicates a high correlation between the actual and predicted values for this model. In addition, a normal probability plot of the residuals was plotted (Fig. 16) to confirm if the normality assumption fitted well with the observed data. If the residuals follow a normal distribution without any obvious pattern, all the points will follow a straight line (Meyer and Krueger, 2001). The plot follows a straight-line pattern, showing a reasonably good fit of the normal probability percentage against standardized residuals.



Fig 14: Pareto graphic analysis for NC



Fig 15: Predicted versus actual values for percent P removal by NC



Fig 16: Normal probability of externally studentized residuals for phosphorus removal by NC

A three-dimensional response surface model was used (Fig. 17) to explain the phosphorus adsorption efficiency influenced by the different variables. A surface plot is useful to plot the relationships between the fitted response obtained from the model and two continuous variables to provide better visualization of the statistically significant factors derived from the statistical analysis. It displays the three-dimensional relationship in two dimensions, with the variables on the x- and y-axes, and the response variable on the z-axis, represented by a smooth surface. The optimal condition to achieve the maximum removal efficiency was obtained as contact time - 16 hours, pH-5, adsorbent dose- 25 g/L, and initial concentration- 5 mg/L. Under these conditions, 91.5% removal efficiency can be achieved with a composite desirability function of 0.977 (very

close to 1) and indicated that the settings would most likely achieve the proposed maximum percent removal.



Fig 17: Response surface plots showing the effect of independent variables (A: initial conc, pH;B: dose, time; C: initial conc, time; D: pH, dose; E: initial conc., dose; on P removal% onto natural clay.

#### **3.3.2** Optimization results for Zr modified Clay

The multi-variable regression model for the response P removal percentage was predicted by the following equation shown as Eq. 13 below:

%P Removal= 24.305 - 16.314 A + 6.386 B + 14.502 C+ 10.566 D - 4.446 AB-8.179 AC -5.533 AD+ 2.858 BC + 6.495 CD+ 1.987 ABD- 1.354 ACD - 2.988 BCD+ 4.394 ABCD (13) Where, A=Initial P Conc in mg/L (5-30); B= adsorbent dose in g/L (0.2-1); C= Contact time in

hour (1-16); D = pH (5-9)

The accuracy of the model was checked by the analysis of variance (ANOVA) and Pareto chart (Fig. 18). The higher F value with the combination of the lower P value (Table A8) indicates that the results are significant (Miller Jr, 1997).

The fitness of the model was evaluated by the value of the coefficient of determination ( $\mathbb{R}^2$ ), adjusted  $\mathbb{R}^2$  and predicted  $\mathbb{R}^2$ . The  $\mathbb{R}^2$  value of 0.916 indicates that the predicted values obtained from the model are a very good fit for the experimental data.  $\mathbb{R}^2$  adjusted value of 0.896 indicates that 89.6% of the total variation in phosphorus adsorption data can be described by the selected model. In the reduced model, the P-value (Table A8) for lack-of-fit is 0.914, which is greater than 0.05, indicating that the lack-of-fit is insignificant relative to the pure error.

Fig19 illustrates the predicted versus experimental (actual) values for % P removal. The R<sup>2</sup> value of 0.991 indicates a high correlation between the actual and predicted values for this model. In addition, a normal probability plot of the residuals (Fig. 20) follows a straight line and thus, confirms normal distribution against standardized residuals (Meyer and Krueger, 2001).

The optimal condition to achieve the maximum removal efficiency by ZrMC was obtained at contact time - 16 hours, pH-5, adsorbent dose- 1 g/L, and initial concentration- 30 mg/L. Under

these conditions, 99.9% removal efficiency can be achieved with a composite desirability function of 0.998 (very close to 1) and indicated that the settings would most likely achieve the proposed maximum percent removal.



Fig 18: Pareto graphic analysis for ZrMC





Fig 19: Predicted versus actual values for percent P removal by ZrMC

Fig 20: Normal probability of externally studentized residuals for phosphorus removal by ZrMC





Fig 21: Response surface plots showing the effect of independent variables (A: initial conc, pH;B: initial conc, time; C: pH, time; D: dose, time; E: pH, dose; F: initial conc., dose; on P removal% onto ZrMC.

## 3.4 Column Experiment

A fixed-bed column was used to perform a continuous adsorption experiment to determine the feasibility and practical use of NC and ZrMC for phosphorus removal. The top of the adsorbent column was fed with a synthetic 5 mg/L "P" solution downward. The breakthrough curves for the adsorbents in column experiments are represented in Fig 22. It shows the loading behaviour of phosphorus as it was removed in the fixed bed column and was expressed in terms of the ratio of the effluent phosphorus concentration to the influent phosphorus concentration (Ct/Co) as a function of time for a given bed height. As shown, the same trend was observed for both adsorbents

with different capacities. When the adsorbents are not saturated at the start of the experiment, the phosphate ions in the feeding solution are completely absorbed by the adsorbent, and the concentration of P in the effluent solution is near to zero. The concentration of P in the output solution began to increase when the adsorbent had been saturated as a result of increasing adsorbent contact with the feeding solution. In both cases, the concentration of P in the outlet solution increased by increasing the time. For both NC and ZrMC column, the concentration of P in outlet solution increased very slowly and after 330 min (3300 mL) started to be flatted. The experiment continued up to 380 min (3800 mL) but still was below breakthrough concentration which indicates both adsorbents perform in column experiment very well (Sun et al., 2014).



Fig. 22: Breakthrough curve in Continuous P removal study by NC and ZrMC calcinated granules.

To explain the phosphorus adsorption in the columns, the Yoon-Nelson model, an adsorption model widely applied to single-component systems was employed. The Yoon-Nelson model parameters ( $K_{YN}$  and  $\tau$ ) were calculated by a plot of ln ( $C_t/C_t-C_i$ ) vs. t using linear regression and presented in Table 5. The  $\tau_{exp}$  amounts were provided from the experimental data. No significant difference was found between the experimental and estimated breakthroughs (Table 5).

Adaanhant	Yoon-Nelson model						
Adsorbent	$K_{YN}$ (min <sup>-1</sup> )	τ <i>(min)</i>	$\tau_{exp}$ (min)	$R^2$	SEE		
NC	0.025	189.1	190	0.898	0.748		
ZrMC	0.021	237.5	210	0.705	0.952		

Table 5: Yoon-Nelson model parameters obtained from breakthrough curve fitting

#### 3.5 Proposed P Adsorption Mechanism

Some complementary tests were conducted to further understand the adsorption processes of P by clay samples. First, the initial pH of the solution before adsorption was measured, as well as the equilibrium pH after adsorption, and the results (Fig 23) revealed that the pH increased after adsorption. In an acidic environment, the release of OH<sup>-</sup> during ligand exchange was mostly responsible for the rise in pH after adsorption. (Boujelben et al., 2014, Tanada et al., 2003, Yoon et al., 2014). As a result, the involvement of the ligand exchange mechanism may be suggested in this adsorption process. In addition, the point of zero charges, pHpzc of the adsorbents before and after P adsorption with different initial concentrations were studied (Fig. 24). The pHpzc of NC after P adsorption shifted from 8.7 to 7.4, and 6.5 at initial P concentrations of 5, and 50 mg/L, respectively. In the case of ZrMC, a similar pattern was observed. The shift in pHpzc toward lower pH values is also a sign of inner-sphere complexation via ligand exchange (Huang et al., 2015, Yoon et al., 2014). The creation of outer-sphere surface complexes, on the other hand, does not affect the surface charge (Su et al., 2013), which indicates that the shift in pHpzc toward lower pH values is a sign of inner-sphere complexation via ligand exchange. The presence of Inner-sphere ligand exchange techniques in the FTIR spectra of the clays before and after phosphorus adsorption is also shown by the FTIR spectra of the clays before and after phosphorus adsorption. The OH stretching vibration of hydroxyl groups and the blending vibration of adsorbed water were attributed to the wide band at 3450 cm<sup>-1</sup> and the peak at 1434 cm<sup>-1</sup>, respectively. (Yu and Chen,

2015, Liu et al., 2010). The bands that were initially been at 3450 cm<sup>-1</sup> after phosphorous adsorption moved to 3480 cm<sup>-1</sup>, confirming the interaction of phosphate with the hydroxyl groups on the adsorbent via ligand exchange. (Liu et al., 2010).



Fig 23: Final pH of the solution at the end of contact using NC and ZrMC



Fig 24: Determination of the pHpzc of the samples using the pH drift method, A: NC; B: ZrMC

## **4** Conclusion and Future Recommendation

This study has shown the potential for the use of natural and modified clay samples as a material for phosphorus removal in wastewater treatment. After the zirconium modification, the maximum adsorption capacity of the modified sample was observed 23 times higher than the natural sample. The adsorbents possessed a high point of zero charges and were able to capture phosphate ions effectively captured in the pH range 2-9 without significant leaching of Zr. The increase in the amount of phosphorus adsorbed was shown to increase sharply as the concentration increased. This is a good characteristic of materials that could have industrial applications for use in wastewater treatment. Similarly, an increase in the amount of adsorbents increases the percent removal of the phosphorus. According to the ANOVA result, the model presents a high R<sup>2</sup> value of 99.92%, which indicates that the accuracy of the polynomial models was good for both models. From the optimization study, 91.5% and 99.9% P removal were obtained by NC and ZrMC respectively. Kinetic study of the equilibrium data showed that the phosphorus adsorption onto the clays followed pseudo-second-order kinetics model and the isotherm result demonstrates that the Langmuir model fits better than Freundlich model, indicating monolayer adsorption of phosphorus by both NC and ZrMC. The adsorbents were shaped in granules and used to investigate their performance in removing phosphorus in fixed bed continuous columns. Like the batch experiments, the breakthrough curves from the column study revealed that the adsorbents are efficient to remove phosphorus in a continuous process as well. However, to use the adsorbents in continuous column process efficiently, further experiments need to be conducted to investigate the effect of different process parameters such as bed height, column diameter, adsorbate flowrate, initial P concentration, and presence of coexisting anions including Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>. In addition, the statistical model needs to be developed for the optimization and prediction of phosphorus removal in a continuous process. In summary, this work proved that the cheap and easily available natural and modified adsorbents acted as a promising adsorbent candidate for efficient and preferable phosphorus removal from contaminated water and could replace various synthetic costly adsorbents. In future, this material may be used to remove other contaminants from an aqueous medium. Furthermore, the possibility of using the phosphorus enriched adsorbents as a slow-release fertilizer source to provide phosphorus for agricultural production can be investigated. In addition, the investigation of regenerability of the modified adsorbents is suggested after considering the detailed cost analysis of the developed product.

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# Appendix

Parameter	Unit	Lagoon wastewater
pН	-	8.02
EC	(µS/cm)	340.5
Al	mg/L	0.14
В	mg/L	0.22
Ca	mg/L	21.6
Cu	mg/L	0.02
Fe	mg/L	0.4
K	mg/L	10.9
Mg	mg/L	6.9
Mn	mg/L	0.21
Na	mg/L	26.5
Р	mg/L	1.290
S	mg/L	1.129
Zn	mg/L	0.0076
F	mg/L	0.05
Cl	mg/L	36.8
NO <sub>2</sub> -	mg/L	0.56
<b>SO</b> <sub>4</sub> <sup>2-</sup>	mg/L	0.16
NO <sub>3</sub> -	mg/L	0.15
PO4 <sup>3-</sup>	mg/L	2.0

Table A 1: The pH, EC and elemental analysis of lagoon wastewater (n=1)

Table A 2: Chemical compositions (in wt%) of natural and modified clay by XRF (n=2)

Component	NC (wt%)±SD	ZrMC (wt%)±SD
SiO <sub>2</sub>	64.39±2.1	55.91±1.7
Al <sub>2</sub> O <sub>3</sub>	12.09±1.4	9.87±1.2
Fe <sub>2</sub> O <sub>3</sub>	6.25±1.1	5.59±1.2
CaO	6.11±1.01	5.13±0.9
K <sub>2</sub> O	$3.52{\pm}0.4$	3.12±0.4
MgO	$2.84{\pm}0.3$	2.81±0.2
SO <sub>3</sub>	$2.48{\pm}0.4$	1.91±0.2
Na <sub>2</sub> O	$0.67{\pm}0.2$	$0.82{\pm}0.2$
$P_2O_5$	0.26±0.1	$0.18{\pm}0.1$
BaO	0.13±0.04	0.12±0.06
$ZrO_2$	$0.03 \pm 0.008$	13.5±1.31

Element	Unit	NC±SD	ZrMC±SD
As	mg/kg	11.7±1.2	10.53±0.9
В	mg/kg	18.4±0.4	56.79±0.5
Ba	mg/kg	268±9.1	322±10.6
Ca	mg/kg	26354±289.2	12486±360
Cd	mg/kg	1.10±0.2	1.15±0.2
Со	mg/kg	1.34±0.3	0.77±0.2
Cr	mg/kg	16.2±1.2	13.17±0.9
Cu	mg/kg	26.3±1.4	26.02±1.9
Fe	mg/kg	25540±255	21222±320
Hg	mg/kg	< 0.003	< 0.003
K	mg/kg	4154±120	2656±97
Mg	mg/kg	8964±452	7074±320
Mn	mg/kg	308±18	294.1±29
Мо	mg/kg	3.8±1.1	2.71±0.8
Na	mg/kg	369±12	885±31
Ni	mg/kg	15.0±2.1	12.0±1.7
Р	mg/kg	651±30	541.1±72
Pb	mg/kg	10.6±0.28	8.43±0.7
Sb	mg/kg	<9	<4.1
Se	mg/kg	<16.5	<9
Sn	mg/kg	<4	<4
U	mg/kg	<14	<14
Zn	mg/kg	85±9.1	74±7.7
Zr	mg/kg	$42.4 \pm 4.1$	123430±480

Table A 3: Trace elements in acid digestate from ICP-OES analysis (70 %(w/w) HNO<sub>3</sub> : 34-37%(w/w) HCl =3:1; digested with digestion blocks (DigiPrep) for 6 hours via automated control of temperatures up to 95 °C); n=3

		Land use						
Substance	Year revised/ released <sup>a</sup>	Agricultural	Residential/ parkland	Commercial	Industrial			
Arsenic (inorganic)	1997	12 <sup>b</sup>	12 <sup>b</sup>	12 <sup>b</sup>	12 <sup>b</sup>			
Barium	1999	750 <sup>c</sup>	500 <sup>c</sup>	2000 <sup>c</sup>	2000 <sup>c</sup>			
Benzene	1997	0.05d	0.5d	5d	5d			
Benzo(a)pyrene	1997	0.1 <sup>e</sup>	0.7 <sup>f</sup>	0.7 <sup>f</sup>	0.7 <sup>f</sup>			
Cadmium	1999	1.4 <sup>b</sup>	10g	22 <sup>b</sup>	22 <sup>b</sup>			
Chromium		h	h	h	h			
Total chromium	1997	640	640	870	870			
Hexavalent chromium (VI)	1999	0.4"	0.4"	1.4"	1.4"			
Copper	1999	63 <sup>0</sup>	630	910	910			
Cyanide (free)	1997	0.9b	0.9 <sup>b</sup>	8.0 <sup>b</sup>	8.0 <sup>b</sup>			
DDT (total)	1999	0.7 <sup>i</sup>	0.7 <sup>i</sup>	12 <sup>i</sup> , j	12 <sup>c,j</sup>			
Ethylbenzene	1997	0.1d	1.2 <sup>h</sup>	20 <sup>h</sup>	20 <sup>h</sup>			
Ethylene glycol	1999	960 <sup>k</sup>	960 <sup>k</sup>	960 <sup>k</sup>	960 <sup>k</sup>			
Lead	1999	70 <sup>b</sup>	140 <sup>b</sup>	260 <sup>b</sup>	600 <sup>b</sup>			
Mercury (inorganic)	1999	6.6 <sup>b</sup>	6.6 <sup>b</sup>	24 <sup>b</sup>	50 <sup>b</sup>			
Naphthalene	1997	0.1 <sup>d</sup>	0.6 <sup>h</sup>	22 <sup>h</sup>	22 <sup>h</sup>			
Nickel	1999	50 <sup>1</sup>	50 <sup>1</sup>	501	50 <sup>1</sup>			
Pentachlorophenol	1997	7.6 <sup>b</sup>	7.6 <sup>b</sup>	7.6 <sup>b</sup>	7.6 <sup>b</sup>			
Phenol	1997	3.8b	3.8b	3.8b	3.8b			
Polychlorinated biphenyls (PCBs)	1999	0.5m	1.31	331, j	33l, j			
Tetrachloroethylene	1997	0.1 <sup>e</sup>	0.2 <sup>f</sup>	0.5f	0.6 <sup>f</sup>			
Thallium	1999	1 <sup>n</sup>	10	10	10			
Toluene	1997	0.1 <sup>e</sup>	0.8f	0.8 <sup>f</sup>	0.8f			
Trichloroethylene	1997	0.1d	3h	31h	31h			
Vanadium	1997	130 <sup>1</sup>	130 <sup>1</sup>	130 <sup>i</sup>	130 <sup>i</sup>			
Xylene	1997	0.1 <sup>e</sup>	1f	17 <sup>f</sup>	20 <sup>f</sup>			
Zinc	1999	200 <sup>1</sup>	2001	3601	3601			

## Table A 4: Canadian soil quality guidelines (mg·kg<sup>-1</sup>) (CCME, 2007)

Notes: SQGE = soil quality guideline for environmental health; SQGE = soil quality guideline for human health.

"Guidelines released in 1997 were originally published in the working document entitled "Recommended Canadian Soil Quality Guidelines" (CCME 1997) and have been revised, edited, and reprinted here. Guidelines revised/released in 1999 are published here for the first time (see Table 2).

<sup>b</sup>Data are sufficient and adequate to calculate an SQG<sub>EH</sub> and an SQG<sub>E</sub>. Therefore the soil quality guideline is the lower of the two and represents a fully integrated de novo guideline for this land use, derived in accordance with the soil protocol (CCME 1996). The corresponding interim soil quality criterion (CCME 1991) is superseded by the soil quality guideline.

<sup>C</sup>Data are insufficient/inadequate to calculate an SQG<sub>HH</sub>, a provisional SQG<sub>HH</sub>, an SQG<sub>E</sub>, or a provisional SQG<sub>E</sub>. Therefore the interim soil quality criterion (CCME 1991) is retained as the soil quality guideline for this land use.

<sup>d</sup>Data are sufficient and adequate to calculate only a provisional SQG<sub>E</sub>. It is greater than the corresponding interim soil quality criterion (CCME 1991). Therefore, in consideration of receptors and/or pathways not examined, the interim soil quality criterion is retained as the soil quality guideline for this land use.

Element	Unit	NC±SD	ZrMC±SD
As	mg/L	< 0.009	< 0.009
В	mg/L	$0.0138 {\pm} 0.0006$	$0.0040\pm0$
Ba	mg/L	$0.0655 \pm 0.0005$	$0.0040 \pm 0.0001$
Ca	mg/L	14.10±1.3	1.354±0.2
Cd	mg/L	< 0.0003	< 0.0003
Co	mg/L	< 0.001	< 0.001
Cr	mg/L	0.0008	< 0.0003
Cu	mg/L	0.001	< 0.001
Fe	mg/L	$0.304 \pm 0.009$	0.016±0
Hg	μg/L	<4.4	<4.4
Κ	mg/L	$1.541 \pm 0.4$	0.119±0.005
Mg	mg/L	$1.865 \pm 0.3$	$0.391 \pm 0.08$
Mn	mg/L	$0.0034 \pm 0.0002$	< 0.0005
Mo	mg/L	$0.0019{\pm}0$	< 0.0014
Na	mg/L	$1.32\pm0.1$	4.60±0.14
Ni	mg/L	< 0.001	< 0.001
Р	mg/L	$0.038 \pm 0.0004$	0.031±0
Pb	mg/L	< 0.003	< 0.003
Sb	mg/L	< 0.0055	< 0.0055
Se	mg/L	< 0.012	< 0.012
Sn	mg/L	< 0.009	< 0.009
U	mg/L	< 0.005	< 0.005
V	mg/L	< 0.002	< 0.002
Zn	mg/L	0.0008±0	< 0.0004
Zr	mg/L	0.0012±0.0004	0.0947±0.003

Table A 5: Leachate analysis of the adsorbents (n=2)

Table A 6: Results from BET Analyzer of NC, and ZrMC

Parameter	NC	ZrMC
Surface area $(m^2/g)$	28.66	109.92
Average pore diameter (A°)	10.08	4.73
Total pores volume (cm <sup>3</sup> /g)	0.070	0.130

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	8	24043.0	3005.38	555.88	0.000
Linear	3	11540.2	3846.72	71.53	0.000
Initial Conc (ppm)	1	3079.8	3079.76	57.27	0.000
Dose (g/L)	1	3668.9	3668.90	68.22	0.000
Time (h)	1	4791.5	4791.51	89.10	0.000
2-Way Interactions	3	9405.6	3135.20	58.30	0.000
Initial Conc (ppm)*Dose (g/L)	1	2857.9	2857.86	53.14	0.000
Initial Conc (ppm)*Time (h)	1	3303.4	3303.37	61.43	0.000
Dose (g/L)*Time (h)	1	3244.4	3244.35	60.33	0.000
3-Way Interactions	1	2877.0	2876.97	53.50	0.000
Initial Conc (ppm)*Dose (g/L)*Time (h)	1	2877.0	2876.97	53.50	0.000
Curvature	1	220.3	220.32	4.10	0.050
Error	41	2204.9	53.78		
Lack-of-Fit	8	1963.9	245.48	33.60	0.450
Pure Error	33	241.1	7.31		
Total	49	26248.0			

 Table A 7: Analysis of Variance (NC) showing different significant parameters and their interactions with each other of the developed model

 Table A 8: Analysis of Variance (ZrMC) showing different significant parameters and their interactions with each other of the developed model

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	14	39866.3	2847.6	813.55	0.000
Linear	4	30186.3	7546.6	1360.98	0.000
Initial Conc (ppm)	1	12775.5	12775.5	2303.99	0.000
рН	1	1957.2	1957.2	352.97	0.000
Dose (g/L)	1	10094.8	10094.8	1820.55	0.000
Time (h)	1	5358.8	5358.8	966.42	0.000
2-Way Interactions	5	8046.6	1609.3	290.23	0.000
Initial Conc (ppm)*pH	1	948.8	948.8	171.12	0.000
Initial Conc (ppm)*Dose (g/L)	1	3210.9	3210.9	579.07	0.000
Initial Conc (ppm)*Time (h)	1	1469.7	1469.7	265.05	0.000
pH*Dose (g/L)	1	392.1	392.1	70.72	0.000
Dose (g/L)*Time (h)	1	2025.0	2025.0	365.20	0.000
3-Way Interactions	3	706.0	235.3	42.44	0.000
Initial Conc (ppm)*pH*Time (h)	1	189.4	189.4	34.16	0.000
Initial Conc (ppm)*Dose (g/L)*Time (h)	1	88.0	88.0	15.86	0.000
pH*Dose (g/L)*Time (h)	1	428.6	428.6	77.30	0.000
4-Way Interactions	1	926.8	926.8	167.15	0.000
Initial Conc (ppm)*pH*Dose (g/L)*Time (h)	1	926.8	926.8	167.15	0.000
Curvature	1	0.5	0.5	0.10	0.756
Error	35	194.1	5.5		
Lack-of-Fit	2	1.0	0.5	0.09	0.914
Pure Error	33	193.0	5.8		
Total	49	40060.4			



Fig A1: XRD analysis of NC and ZrMC



Fig A2: Thermogravimetric analysis of NC and ZrMC (with  $10^0 \mbox{C/min}$  heating rate in  $N_2$ 

atmosphere)


Fig A3: Scanning electronic microscope (SEM) of NC; (A) 10 μm image, (B) 20 μm image, (C) 50 μm image, (D) 100 μm image.



Fig A4: Scanning electronic microscope (SEM) of ZrMC; (A) 10 µm image, (B) 20 µm image,

(C) 50 µm image, (D) 100 µm image.



FigA5: FTIR Analysis of NC