Engineered Geomedia Kaolin Clay-Reduced Graphene Oxide–Polymer Composite for the Remediation of Olaquindox from Water

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ABSTRACT: Globally, there is an upsurge in the use of unregulated veterinary pharmaceuticals with enhanced release into the environment, resulting in water pollution, which is difficult to remediate. To address this issue, we synthesized and characterized highly hydrophobic three-dimensional ordered engineered geomedia with multiple channels. Kaolin clay (K) was functionalized with either graphene oxide (GO) synthesized via Tour’s method or reduced GO in situ with covalently linked methoxyether polyethylene glycol (GO-PEG) using a simple and easily scalable amidation reaction. This was done to enhance the adsorption of olaquindox, a veterinary antibiotic. The X-ray diffraction profile confirmed the grafting of GO and GO-PEG to kaolin. Morphological analysis revealed the architecture of thin films of GO/GO-PEG grafted on the kaolin surface with extensive porosity. Energy-dispersive X-ray mapping, infra-red spectra, and elemental analysis confirmed the successful synthesis of the engineered geomedia composite of K, GO/rGO, and PEG (KrGO-PEG). Due to multiple surface functional groups of polyamide and amido-carbonic groups on the KrGO-PEG composite, it was suitable for olaquindox adsorption. In batch sorption studies of 0.5XKrO-PEG, the effect of pH (2−10) was negligible but with fast equilibrium time (2−1440 min) at 30 min, while the kinetics and equilibrium data suited the pseudo-second order and Langmuir models, respectively. The maximum adsorption value obtained for the composite was 59.5 mg/g; the higher the GO content, the higher the adsorption. The sorption mechanism was majorly through hydrophobic and π−π interactions. Regenerated/reused adsorbents after 4 cycles had the same efficacy in remediating olaquindox from simulated/real water.

1. INTRODUCTION

Pharmaceuticals are referred to as emerging contaminants because of their persistence in environmental media.1 However, a specific group of pharmaceuticals that have gained notoriety are veterinary pharmaceuticals (VPs).2 These kinds of pharmaceuticals are problematic, because unlike some human pharmaceuticals with regulated use, most VPs are used indiscriminately without any regulation.3 A study conducted by Martínez-Carballo and co-workers4 estimates that one-third of pharmaceuticals used in Europe are veterinary related. Environmental pollution from VPs stems from their breakdown product/metabolites in the environment after application.5 Farming activity represents a major source of release into the environment.5 Other sources are from hospitals/clinics, animal shelters, and abattoirs.1,5 In animals, veterinary antibiotics serve two main purposes: as a growth promoter and to counteract infections.8 Bacterial resistance, a common occurrence recently, is attributed to VP use as a growth enhancer, resulting in destruction of the therapeutic efficacy of drugs and the antioxidant defense system of animals.9 As a result, in Europe, there is a ban on some growth hormones for animals including olaquindox.8 Olaquindox is an antibiotic belonging to the quinoxaline group (Figure 1) and is therapeutically administered in pigs, fishes, and chicken.10 Olaquindox has been used as an anticancer, antiepileptic, analgesic, anti-inflammatory, and antiviral drug.11 Despite the ban on olaquindox due to its negative effects, such as

Figure 1. Structure of olaquindox.
genotoxicity, carcinogenicity, phototoxicity, mutagenicity, and renal toxicity, it is still being used in several parts of the world, South Africa inclusive.\(^{12}\) Olaquindox is often discharged indiscriminately into conventional wastewater treatment plants, which lack the capacity for effective remediation.\(^{6}\) Therefore, the need arises to develop effective techniques for remediation. Techniques such as biodegradation, membrane filtration, electrochemistry, and adsorption have been applied in its remediation from wastewater. Nonetheless, adsorption is most effective because of advantages such as ease of use, non-generation of toxic byproducts, and low cost. For instance, olaquindox has been adsorbed with carbonaceous materials such as carbon nanotubes, modified chitosan, and soil.\(^{13}\) However, these adsorbents had issues such as interference from coexisting molecules, low adsorption capacity, slow olaquindox uptake rates, and high cost. In a bid to overcome these challenges, it is imperative to develop chemically versatile adsorbent materials that are cheap and from natural sources. Adsorbents such as engineered geomaedia (polymer-modified clay composite), clay, activated carbon, graphene/graphene oxide (GO), and MXenes\(^{14}\) (two-dimensional layer nanomaterials consisting of transition metal nitrides, carbides, and carbonitrides) synthesized with green techniques are essential for the remediation of olaquindox and other pharmaceuticals.

Graphene-based materials (GO) possess outstanding properties as adsorbents due to high surface area of approximately 2630 m\(^2\)/g.\(^{15}\) GO contains numerous oxygen and carbon functional groups. Nonetheless, GO/reduced GO (rGO) do not achieve high adsorption capacity because of aggregation in wastewater, which constricts surface area.\(^{16}\) Aggregation of GO/rGO during adsorption occurs due to interplanar interaction of graphene sheets. The hydrophilic nature of GO causes difficulty in separation from adsorbate solution.\(^{17}\) To overcome aggregation/separation, GO is anchored on a solid support, ensuring that adsorption capacity is maximized, and separation issues are eliminated. Studies show that anchoring GO on support materials led to increased adsorption of metals and pharmaceuticals.\(^{18}\) Therefore, we propose clay geomaedia as an anchor for GO/rGO. Clays (montmorillonite and kaolin) are structurally similar to mesoporous silica. However, clays possess aluminosilicate components in varying proportions.

Kaolin occurs naturally and is used in industrial, environmental, and agricultural applications because of properties such as good surface area, mechanical and thermal stability.\(^{19}\) Structurally, kaolin comprises two interconnected layers: the octahedral AlO\(_2\)(OH)\(_4\) and tetrahedral SiO\(_4\) layers.\(^{20}\) Kaolinite has been applied in adsorption of organics such as dyes, persistent organic pollutants, and pharmaceuticals.\(^{21}\) An issue with kaolin is low sorption capacity and, hence, the need for modification.\(^{21}\) Therefore, we aim to fabricate hybrid engineered geomaedia with the base as kaolin and a highly hydrophobic amido-carbon super web-like structure for enhanced adsorption. This modification ensures that the resultant hybrid modified clay (adsorbent) has a good separation/super adsorptive property. Furthermore, the modification improves dispersion and adsorption increases due to improved surface coverage.\(^{22,23}\) Clays have been modified with organic functional groups such as ionic liquids\(^{24,25}\) and GO.\(^{25}\)

To further increase the adsorption capacity of kaolin for olaquindox, we propose an expansion of GO with a polymer and covalently attach it to kaolin. Polymers such as polycrylates, polyvinylesters, and polyvinyl chloride structure have been used in numerous applications.\(^{26,27}\) Methoxyether polyethylene glycol (PEG) is a hydrophilic polymer with molecular similarities to polyethyleneimine, and its adsorption mechanism for organics is through hydrophobic and \(\pi-\pi\) interactions.\(^{28}\) PEG is potentially suitable for adsorption in water because it is highly biocompatible, biologically inert, has low toxicity, and is highly soluble in water.\(^{29}\) However, there are limited reports of PEG in water treatment\(^{30}\) but extensive use in drug delivery.\(^{28}\) PEG consists of a gigantic system of C, H, and O atoms with extensive surface functionalization tendencies by chemical/thermal reduction to become more hydrophobic. The reaction between GO and PEG is facilitated by the interaction of carboxylic acid and hydroxyl groups, which results in a highly ordered crystalline material.\(^{31}\) Olaquindox remediation requires an adsorbent with fast/easy separation and regeneration with optimized multisurface functional groups.

To address these issues, we developed an ecofriendly easily scalable method for the synthesis of multifaceted functional adsorbents with environmentally benign chemicals and a kaolin base. Multifunctional carboxylic groups anchored on kaolin stem from the r(GO)/PEG superstructure, which will be efficient in remediating olaquindox. GO has multioxygen functional groups on its surface, which if reduced can be effective in adsorption, with kaolin as the base/anchor for r(GO) and PEG. PEG molecules interact with GO via a ring opening reaction resulting in an expanded molecular architecture and grafted on kaolin. To the best of the authors’ knowledge, the anchoring of GO-PEG and its in-situ reduction on clay and application in remediation of olaquindox from simulated/real water has not been carried. The hybrid adsorbents were characterized and applied in batch adsorption of olaquindox from real and simulated water samples.

2. EXPERIMENTAL SECTION

2.1. Materials. N-(3-(Dimethylamino)propyl)-N-ethylcarbodiimide (EDC), methoxy polyethylene glycol (mPEG), glutaraldehyde, high-performance liquid chromatography (HPLC) grade methanol, hydrazine hydrate, graphite powder, HCl (32%), kaolinite, N-hydrosuccinimide (NHS), and olaquindox were purchased from Aldrich and utilized without any further purification.

2.2. Synthesis of K-NH\(_2\) GO, GO-PEG, KGO, and K(r)GO-PEG. Amine-functionalized kaolin clay (K-NH\(_2\)) was synthesized as previously reported.\(^{32}\)

2.2.1. GO-PEG Synthesis. Initially, GO synthesis was via Tour’s method.\(^{33}\) Already sonicated (2 h) GO was used in GO-PEG synthesis. NHS and EDC were added to GO, which served as the crosslinking agent. Different ratios of PEG were added to the mixture in a three-neck flask and stirred at room temperature for 24 h. The resulting hydrogel mixture was rinsed to remove any remaining unattached GO/PEG and freeze dried. PEG molar ratios of 0.10 PEG, 0.25 PEG, and 0.50 PEG were applied as a precursor for 0.10 GO-PEG, 0.25 GO-PEG, and 0.5 GO-PEG with the PEG ratio assigned as “X” in adsorbent materials.

2.2.2. XKGO-PEG/VKrGO-PEG Synthesis. This was achieved by stirring about 1.0 g of K-NH\(_2\) with GO-PEG, while pH was adjusted to neutral using drops of ammonium hydroxide. Subsequently, glutaraldehyde (2 mL) was added, which served as a crosslinking agent. The resultant product was washed with water to a neutral pH and dried in an oven at 50 °C for 6 h. A
similar process was applied for XKrGO-PEG, but the temperature was set at 80 °C, and hydrazine hydrate was added as a chemical reducing agent. The reactants were subsequently stirred for 8 h, and the product was filtered and washed with ultrapure water to a pH of 7 and freeze dried before application.

2.3. Adsorbent Characterization. X-ray diffraction (XRD) analysis was carried out using a Bruker D8 Advance instrument with a Cu Kα source of radiation in 2 theta range 10−90°. Fourier-transform infrared (FTIR) analysis was carried out using a PerkinElmer Spectrum 100 series with an attenuated total reflectance accessory in the 4000−400 cm⁻¹ range. Structural morphology was analyzed with the aid of a Zeiss 10 kV field emission scanning electron microscope (FESEM) and high-resolution transmission electron microscope (HRTEM, JEOL 2100). Energy-dispersive X-ray (EDX) analysis aided elemental determination and adsorbent mapping. Pore sizes, pore diameters, and surface area were analyzed with Micromeritics Tristar II 3020 equipment. Samples were degassed for 12 h at 90 °C. A Malvern Zetasizer Nanoseries NanoZs with a dip cell was used in obtaining zeta potential values. Thermogravimetric analysis was carried out in an inert environment. Elemental analysis was carried out using a Thermo Scientific CHNS/O analyzer.

2.4. Analytical Method. Olaquindox was quantified with a Shimadzu Prominence with a 2 LC-20 AD XR pump with a UV−visible detector. The detection wavelength was 240 nm, and separation was carried out using an Agilent Eclispe XDB C-18 column (46 × 150 mm, 5 μm particle size) under isocratic conditions. The solvent system employed was methanol/water (50:50) with an injection volume of 20 μL and a 1.0 mL min⁻¹ flow rate.

2.5. Adsorption Studies. Duplicate batch adsorption studies were carried out with olaquindox solution (20 mL, 15 mg/L) by agitating using a temperature-controlled electric shaker. Studies on the effects of pH, dose, contact time, kinetics, and isotherm were carried out. The pH studies were carried out by adjusting the olaquindox solution within a range of 2−10 with 0.01 M NaOH/HCl. Dose optimization experiments were carried using 5−50 mg adsorbent mass in 20 mL of the adsorbents for a period. Kinetic experiments were carried out to ascertain the quantity of olaquindox adsorbed per time at optimum pH and different concentrations of the solution (30−90 mg L⁻¹) using an adsorbent mass of 150 mg. Intermittently, 1 mL of solution was withdrawn (from the adsorbent/olaquindox aliquot) between 2 and 1440 min and the concentration was determined.

Olaquindox adsorbed (mg g⁻¹) was determined (using eq 1) from the adsorption per gram of geomedia at specific time:

\[
q_e = \frac{(C_o - C_e)V}{W}
\]  

(1)

where \( q_e \) is the concentration at equilibrium, \( W \) is mass of adsorbent (g), \( V \) is volume of solution (L), and \( C_o \) and \( C_e \) are initial concentration and final concentration at time \( t \) (mg/L). Removal percentage was determined using eq 2:

\[
\text{%removal} = 100 \times \frac{C_o - C_e}{C_o}
\]  

(2)
Table 1. Textural Properties and Elemental Composition of KGO and KrGO-PEG Geomedia

| element/textural properties | GO | kaolin | KGO | 0.1KrGO-PEG | 0.25KrGO-PEG | 0.5KrGO-PEG |
|-----------------------------|----|--------|-----|-------------|-------------|-------------|
| C                           | 37.6 | 2.43 | 7.88 | 18.5 | 25.4 | 28.5 |
| H                           | 2.23 | 2.43 | 2.82 | 3.86 | 5.17 | 5.65 |
| N                           | 0.58 | 1.84 | 2.18 | 1.84 | 0.96 | 0.72 |
| O                           | 59.5 | 75.8 | 86.6 | 75.8 | 68.5 | 65.2 |
| H/C                         | 0.71 | 2.5  | 4.29 | 2.5  | 2.44 | 2.36 |
| O/C                         | 1.75 | 5.44 | 14.6 | 5.44 | 3.59 | 3.04 |
| N/C                         | 0.0087 | 0.06 | 0.16 | 0.06 | 0.02 | 0.015 |
| SA (m² g⁻¹)                 | 39  | 10.4  | 5.49 | 5.36 | 5.34 | 5.26 |
| pore vol (cm³ g⁻¹)          | 0.016 | 0.04 | 0.065 | 0.06 | 0.06 | 0.06 |
| pore size (nm)              | 4.2 | 14.7  | 14.6 | 9.84 | 9.2  | 8.86 |

**Experimental data obtained from the sorption rate experiments were fitted into the pseudo-first order (PFO), pseudo-second order (PSO), and intraparticle diffusion (IPD) models. The equations are presented (Table S1, kinetic models).**

 Isotherm analysis was carried out by evaluating the equilibrium data using isotherm models such as Freundlich, Langmuir, Temkin, and Dubinin–Radushkevich (DR) (Table S2, adsorption isotherm models).

 For carrying out the thermodynamic experiments, 30 mg of adsorbent materials was placed in olaquindox solution and agitated at 298, 308, and 318 K for a period of 24 h. Afterward, the adsorbate solutions were filtered with a 0.45 μm cellulose acetate filter and the concentration was quantified with HPLC. This process was repeated 4 times.

2.6. Regeneration Studies. In regeneration studies, adsorbents were loaded with olaquindox at its natural pH at room temperature (25 °C). Subsequently, adsorbents were washed with acidic ethanol with a thermostatic shaker for 3 h to desorb the bound olaquindox from the adsorbent, which was dried in a vacuum oven at 60 °C. The desorbed adsorbate solution was filtered, and the concentration of the filtrate was quantified with HPLC. This process was repeated 4 times.

2.7. Statistical Analysis. Nonlinear regression equations in Origin 2018 were used for data analysis of kinetic and isotherm models. The appropriateness of the model that most fits the experimental data was chosen based on the values of the least sums of squares (SSE) and residual square errors (RSE).

3. RESULTS AND DISCUSSION

3.1. Characterization of Adsorbents. The FTIR spectral analysis was carried out to determine the various functional groups present on the kaolin and the modified geomedia (Figure 2a). Typical silicon-related functional peaks of the pristine kaolin were observed at 991, 521, and 456 cm⁻¹, and these were attributed to horizontal stretching of siloxane (Si–O) bonds, Si–O–Si, and Si–O–Al bending vibrations, respectively. The −OH bending vibrations on Al–Al–OH and Al–Mg–OH were recorded at 788 and 909 cm⁻¹, respectively. The −OH stretching vibrations of physically adsorbed water on kaolin interlayer spaces and those bound to the kaolin surface appeared at 1637 and 3600 cm⁻¹, respectively. The GO surface was dominated by oxygen functional groups, which acts as an anchor for further modification via reactions such as ring opening and/or esterification via epoxy or carboxyl functional groups. The −C=O– stretching vibrations from carboxyl and carbonyl functional groups were observed at 1725 cm⁻¹, while vibrations of the −C=C– and −C–C– bonds of the GO graphitic framework were at 1634 and 1572 cm⁻¹, respectively. The −C–OH and C–O stretching vibrations were observed at 1389 and 1068 cm⁻¹, respectively. KGO had hybrid absorption vibrations that were reflective of its precursors (GO and kaolin), however, there were new peaks and a shift in peak positions for Si–O–Si (459 cm⁻¹) and Si–O–Al (531 cm⁻¹) bending vibrations. The peak at 796 cm⁻¹ (O–Si–O bending vibration) was attributed to quartz in kaolin. XKrGO-PEG, new peaks appeared after amidation of GO-PEG and kaolin, for instance at 1614 cm⁻¹ ascribed to the −NH–CO– due to amide bond formation, and others at 2871 and 1111 cm⁻¹, indicating that PEG molecules were anchored on the GO surface. The vibrations attributed to −C=H– stretch of alkyl chains and Al–Mg–OH/Al–Mg–OC bonds were present at 2871 and 1030 cm⁻¹, respectively, while the peaks between 1350 and 1450 cm⁻¹ were assigned to amide stretching vibrations from the vinyl group of PEG on XKrGO-PEG. The −N–H– vibration was recorded around 3361 cm⁻¹. The presence of antisymmetric stretching of −N–C– bonds together with out-of-plane NH and NH₂ bonds allowed the geomedia to behave as an H-bond acceptor, as well as an H-bond donor. The analysis of these spectra showed a successful fabrication of the geomedia.

The XRD profile (Figure 2b) of pristine kaolin indicates the presence of kaolinite (aluminum silicate hydroxyl) 1Md structure (JCPDS 00-006-0221). Reflections appeared at 2θ = 12.31°, 19.80° (multiple reflections), 24.85°, 34.95° (multiple reflections), and 38.42° (multiple reflections) corresponding to 001, 020, 002, −201, and −202 planes, respectively. The strong reflection at 2θ = 26.5° and the weaker ones at 40.87, 45.57, and 55.08 were ascribed to quartz and tetrahedral silicate sheets, respectively. At 2θ, the GO diffractogram had an intense reflection peak of 9.76° and interplanar basal spacing of 8.71 Å. This indicates the manifestation of oxygen functionalities and the oxidation of graphite to GO. The modified adsorbents had similar profiles to pristine kaolin, however, with reduced peak intensity. A slight reduction of interlayer spacing in kaolin was observed when (r)GO-PEG loads were increased, which was attributed to the grafting of (r)GO-PEG sheets on kaolin. The reduction in peak intensity and the shift in the 2θ value of kaolin from 12.31 to 12.35, 12.41, 12.43, and 12.45° for KGO, 0.1KrGO-PEG, 0.25KrGO-PEG, and 0.5KrGO-PEG, respectively, were due to the grafting of GO-PEG in the expanded octahedral and...
tetrahedral kaolin structure. This caused a reduction of the interlayer spaces in rGO sheets due to the formation of novel functionalities, from the reduction reaction of hydrazine hydrate on the bulky GO-PEG molecules and the elimination of some pre-existing functional groups. The absence of rGO-PEG XRD peaks for the modified materials indicated that rGO-PEG was homogeneously distributed in XKrGO-PEG.

In a bid to determine the textural properties of the engineered geomedia, N$_2$ adsorption−desorption isotherm/pore size distribution plots (Figure 2c) were obtained with detailed analysis of plots (Table 1). All synthesized adsorbents had reversible type IV IUPAC isotherm, which is typical for predominantly mesoporous materials and an H3 hysteresis loop, except for pristine kaolin, which had H2. Such materials have a highly interconnected architectural framework and are porous. In contrast, H2 type loops are characterized by disorderliness and their pore shapes are irregular with bottle neck constrictions. There was a sharp inflection at adsorption volume beyond the relative pressure $p/p_0$ at 0.4 for XKrGO-PEG as compared to pristine kaolin. This is an indication that GO-PEG was grafted successfully on to kaolin. XKrGO-PEG exhibited increased surface area as compared to kaolin due to the partial reduction of GO-PEG present on kaolin. This indicates that in addition to the functional groups present, adsorption may take place synergistically via the pore and the surface area of the adsorbents.

Elemental analyses of the engineered geomedia are presented in Table 1. For this calculation, only percentages of C, H, N, and O were used. Other elements present in the clay mineral were not considered. K-GO had higher O/C and H/C values as compared to XKrGO-PEG. This implied that XKrGO-PEG was more hydrophobic as compared to K-GO and the hydrophobicity increased as the (H/C, O/C) values reduced with the corresponding increase in GO-PEG concentration. Also observed was the presence of a significant amount of N (amide) in XKrGO-PEG samples, which was due to the amidation reaction. This was supported by the absence of N in pristine kaolin. FTIR peaks at approximately 2860 and 1130 cm$^{-1}$ further serve as a confirmation of the successful covalent attachment of amide functionalities on XKrGO-PEG from the GO-PEG molecules. To further confirm the hydrophobicity of the adsorbent, N/C reduced as the GO-PEG concentration increased. This result implied that 0.5KrGO-PEG is the most hydrophobic among the adsorbents.

Detailed microstructural and morphological analyses of the adsorbents were carried out with FESEM and HRTEM (Figures 3 and 4). SEM images of the adsorbents are shown in Figure 3a−f. GO (Figure 3b) appeared as a rough wrinkled-
like agglomerated sheet. The SEM micrograph of kaolin (Figure 3b) was characterized by irregularly ordered tubular aggregates of varying sizes, which may be linked to distortion in the octahedral layer caused by the replacement of iron with aluminum. These aggregates are rolled up along the edges with sizes between 1 and 10 μm. K-GO- and KKrGO-PEG-modified adsorbent materials (Figure 3c−f) had similar micrographs; however, the presence of a web-like cover of GO and (r)GO-PEG can be seen embedded on and between stacks of kaolin. This confirms that GO/(r)GO-PEG was not only grafted in the interlayer of kaolin but also on the external surface. This anchoring/grafting of GO/(r)GO-PEG on kaolin was further confirmed by examination of the HRTEM micrographs (Figure 4a−f). HRTEM revealed kaolin to be highly crystalline in nature with long distinct irregularly shaped definite tubular-like blocks with sharp edges (Figure 4a). In GO/(r)GO-PEG-modified kaolin micrographs, large blocks of kaolin can be observed with darker spots where wrinkled transparent GO/(r)GO-PEG sheets were layered on dense blocks of kaolin crystals. This is indicative of a successful

Figure 5. (a) EDX spectra, (b) micrograph, and (c) map of 0.5KrGO-PEG geomedia.

Figure 6. Effect of zeta potential and adsorption efficiency of olaquindox at varying pH: (a) kaolin, (b) KGO, (c) 0.1KrGO-PEG, (d) 0.25KrGO-PEG, and (e) 0.5KrGO-PEG.
3.2. Adsorption Studies. Adsorbent textural properties such as the pore diameter, volume, and surface significantly affect adsorption capacity. It was observed (Table 1) that an increase in GO-PEG concentration resulted in an increase in textural properties such as pore size/diameter, which will enhance the uptake of large pollutant molecules within the mesopores. Though the surface areas of the geomedia were slightly lowered, this was due to agglomeration of GO sheets attached on kaolin during the drying process. Thus, it is expected that optimal adsorption capacity will be attained as more amide and carboxyl functional groups (due to GO reduction) in adsorption across the pH range indicate that multiple factors/mechanisms could have been responsible for olaquindox removal. Hence, pH 2 was noted as the optimal pH; however, since pH did not significantly affect adsorption, we opted to use the natural pH (4.9) of olaquindox solution in subsequent experiments. At pH 2, the rich electron surface of olaquindox molecules were neutral, the slight changes in pH resulted in reduced water permeability and increased organic pollutant retention.

Table 2. Kinetic Parameters for the Adsorption of Olaquindox onto Engineered Geomedia

| model | parameter          | KGO | 0.1XKrGO-PEG | 0.25XKrGO-PEG | 0.5XKrGO-PEG |
|-------|--------------------|-----|--------------|---------------|--------------|
| PFO   | $q_e$/mg/g        | 6.62| 11.12        | 18.8          | 22.5         |
|       | $k_p$/min$^{-1}$  | 3.7 | 3.32         | 3.34          | 5.07         |
| PFO   | $q_e$/mg/g        | 6.1 | 10.5         | 17.7          | 21.09        |
| RSE   |                    | 8.24| 5.92         | 22.34         | 20.51        |
| SSR   |                    | 295.05| 844.2       | 525.4         | 3889 |
| PSO   | $k_p$/min$^{-1}$  | 7.41| 3.83         | 2.37          | 0.509        |
| PSO   | $q_e$/mg/g        | 6.3 | 11.3         | 19            | 22.6         |
| IPD   |                    | 11.94| 8.59         | 30.3          | 20.51        |
| IPD   |                    | 291.3604| 841.528   | 2382.175      | 3889         |
| SSR   |                    | 43.548| 83.195       | 223.95        | 240.6        |
| SSR   |                    | 259.7533| 766.9272    | 2188.527      | 3669         |

"RSE, residual sums of square; SSE, sums of square; Nd, not determined.

### 3.3. Effect of pH

The role of pH in adsorption is vital, as it affects surface functional groups of the adsorbent, the adsorbate species in solution, and ultimately adsorption capacity. The effect of pH on olaquindox adsorption (Figure 6) showed that there was only a slight decrease in percentage adsorption across the pH range 2−10. Changes in pH resulted in the protonation−deprotonation transition of the functional groups on olaquindox resulting in chemical speciation of its ionizable compounds. Olaquindox is amphoter in nature because it possesses both amino and hydroxyl functional groups; therefore, it is characterized by two pKₐ values (1.92 and 13.75). In solution, olaquindox exists as three chemical species. At pH below 1.92, olaquindox is a cation, at pH 1.92−13.75, it is a zwitterionic neutral molecule with no charge, and at pH above 13.75, it exists as an anion in solution. Therefore, in the pH range studied (2−10), it was imperative that no significant changes in percentage removal occurred as olaquindox was neutral in solution with lowered affinity for electrostatic attraction or repulsion by the adsorbent. It was observed that as the GO-PEG concentration in the samples increased, removal efficiency also increased. This phenomenon could be attributed to reduced oxygen functional groups with a tendency to form water clusters and increasing carbon functionalities in XKrGO-PEG, which increases hydrophobicity and causes improved adsorption. The improved hydrophobicity of the hitherto hydrophilic GO-PEG molecules on XKrGO-PEG adsorbents can be attributed to their chemical reduction resulting in reduced water permeability and increased organic pollutant retention.

Results for TGA (Supporting Information thermogravimetric analysis, Figure S1) and Raman spectroscopy analysis (Supporting Information Raman spectroscopy analysis, Figure S2) also proved that clay−polymer composite synthesis was successful. Therefore, in the pH range studied, it was expected that adsorbent surfaces will be positively charged. Though the olaquindox molecules were neutral, the slight changes in pH across the pH range indicate that multiple factors/mechanisms could have been responsible for olaquindox removal. Hence, pH 2 was noted as the optimal pH; however, since pH did not significantly affect adsorption, we opted to use the natural pH (4.9) of olaquindox solution in subsequent experiments. At pH 2, the rich electron surface of the adsorbents promotes a certain π-electron reaction, where the adsorbent acts as the π electron donor and the adsorbate as the π electron acceptor. As the pH increased, there was slight reduction in percentage adsorption, which may be attributed to nitrogen group abstraction from olaquindox, which further reinforces the idea of multiple mechanisms. This implies that sorption predominantly took place via hydrophobic interaction and to a lesser extent through H-bond formation between the olaquindox and geomedia. The slight dip in percentage adsorption at basic pH could be attributed to the increasing negative surface of adsorbents and adsorbate solution, which could result in deprotonation of several functional groups, such as hydroxyl, carboxyl, amine, and amide functional groups. Hence, there is a slight repulsion between the adsorbate and the adsorbent molecules in solution. For these reasons, we...
have chosen hydrogen bonding, hydrophobic interactions, and \( \pi-\pi \) interactions as our mechanism for adsorption of olaquindox on to XKrGO-PEG. This is because both olaquindox and our adsorbents have benzene rings and double bonds (–C=–C; –C=O). These geomedia polymeric adsorbents were found to be efficient across the pH spectrum from 2 to 10, ensuring that it would be successful for the remediation of olaquindox in real water samples via \( \pi-\pi \) and hydrophobic interactions.

### 3.4. Effect of Contact Time and Kinetics.

In a bid to determine the adsorption rate, capacity, and mechanisms of the adsorbents, kinetic studies were carried out. In wastewater treatment, rapid removal of pollutants is essential. The optimal contact time for all adsorbents to adsorb olaquindox occurred before 30 min (Supporting Information 4, Figure S4). Initially, there was rapid adsorption of the adsorbate molecules because of vacant sorption sites on the adsorbents, followed by a slow pace leveling off after sorption sites became occupied. Such extremely rapid kinetics are attributed to mesoporosity and several functional groups from the GO-PEG molecules grafted on kaolin with 0.5KrGO-PEG having the most adsorption because it is the most hydrophobic.

Kinetic models such as the PFO, PSO, and IPD (Supporting Information 5 effect of kinetics, Figure S5) were applied to evaluate the adsorption efficiency process. The kinetic parameter results obtained by fitting experimental data into the models are shown (Table 2).

The suitability of the model that most describes the experimental data was selected based on the least SSE and RSE. In contrast to the PFO model, experimental data obtained (\( q_t \), RSE, and SSE) were better fitted to the PSO model. The PSO model in wastewater remediation explains that the adsorption of pollutants from aqueous systems is attributed to electrostatic interaction, which depends on the available and accessible sorption sites at the solid–solution interface; for the GO-incorporated adsorbents, this interaction may not necessarily involve exchange of electrons but between benzene rings in olaquindox and those of the GO sheets. It is also suggested that electrostatic interactions from between charged sites in olaquindox and the amide, amine, and carboxyl functional groups present on XKrGO-PEG adsorbents were present. This may explain the superior adsorption capacity of 0.5KrGO-PEG (22.5 mg/g) and rate constant \( k_2 = 5.09 \times 10^{-5} \) compared to other geomedia. Increasing boundary thickness \( C \) (Table 2) was observed as the GO-PEG concentration was increased with the thickness significantly impacting adsorption of olaquindox on to XKrGO-PEG. This may be an indication that subsequent molecules of olaquindox were able to adsorb onto already adsorbed olaquindox molecules on the adsorbent surface.

### Table 3. Isotherm Parameters of Isotherm for the Adsorption of Olaquindox onto Engineered Geomedia

| adsorbent | KGO | 0.1KrGOPEG | 0.25KrGOPEG | 0.5KrGOPEG |
|-----------|-----|------------|-------------|------------|
| \( q_m \) (mg/g) | 17.43 | 17.76 | 18.83 | 31.04 | 33.63 | 33.33 |
| \( b \) (L/g) | 0.128 | 0.1343 | 0.123 | 0.12155 | 0.12275 | 0.11383 |
| RSE | 23.74 | 23.11 | 22.89 | 45.53 | 49.73 | 45.97 |
| SSE | 2622.06 | 2746.18 | 3026.32 | 8202 | 9651 | 9315 |
| Freundlich | | | | | |
| \( K_f \) (mg/g/(mg/L)^1/n) | 8.22 | 8.45 | 8.63 | 14.1 | 14.58 | 15.2 |
| \( N \) | 0.1216 | 0.12088 | 0.126 | 0.1287 | 0.134 | 0.129 |
| RSE | 59.01 | 58.717 | 60.488 | 145.037 | 151.75 | 175.119 |
| SSE | 2586.742 | 2710 | 2988 | 8103.523 | 7210 | 9526 |
| DR | | | | | |
| \( E \) (kJ/mol) | 1.84 | Nd | Nd | 2.57 | Nd | Nd |
| \( q_0 \) (mg/g) | 0.86 | Nd | Nd | 1.84 | Nd | Nd |
| \( B \) (mol/kJ^2) | 2.0 × 10^{-7} | Nd | Nd | 4.0 × 10^{-7} | Nd | Nd |
| RSE | 54.52 | Nd | Nd | 60.25 | Nd | Nd |

**Note:**
- RSE, residual sums of square; SSE, sums of square; Nd, not determined.

**RSE**
Table 4. Langmuir (Qm) Compared to Other Adsorbents

| adsorbent       | isotherm model | kinetic model | SBET m²/g | qm (mg/g) | equil. time (min) | pH  | reference |
|-----------------|----------------|---------------|-----------|-----------|-------------------|-----|-----------|
| CNT             | Langmuir       | PSO           | 500       | 133.1     | 3                 | 5.3 | 6         |
| MIP             | Langmuir       | PSO           | NA        | 9.62      | 180               | NA  | 54        |
| EPI-chitosan    | Langmuir       | PSO           | NA        | 11        | 180               | NA  | 55        |
| MIP             | Langmuir       | NA            | NA        | 7.86      | 180               | 7.7 | 56        |
| k-GO            | Langmuir       | PSO           | 11        | 18.8      | 30                | 4.9 | this study|
| 0.1KrGO-PEG     | Langmuir       | PSO           | 5         | 33.3      | 30                | 4.9 | this study|
| 0.25KrGO-PEG    | Langmuir       | PSO           | 3         | 47.7      | 30                | 4.9 | this study|
| 0.5KrGO-PEG     | Langmuir       | PSO           | 2         | 59.5      | 30                | 4.9 | this study|
| k-GO            | Langmuir       | PSO           | 7.86      | 180       | 7.7               | 56  | NA        |
| MIP             | Langmuir       | NA            | 11        | 18.8      | 30                | 4.9 | this study|
| EPI-chitosan    | Langmuir       | NA            | 7.86      | 180       | 7.7               | 56  | NA        |
| CNT             | Langmuir       | PSO           | 500       | 133.1     | 3                 | 5.3 | 6         |
| MIP             | Langmuir       | NA            | 7.86      | 180       | 7.7               | 56  | NA        |
| MIP             | Langmuir       | NA            | NA        | 7.86      | 180               | 7.7 | NA        |
| EPI-chitosan    | Langmuir       | NA            | 7.86      | 180       | 7.7               | 56  | NA        |
| k-GO            | Langmuir       | PSO           | 11        | 18.8      | 30                | 4.9 | this study|
| 0.1KrGO-PEG     | Langmuir       | PSO           | 5         | 33.3      | 30                | 4.9 | this study|
| 0.25KrGO-PEG    | Langmuir       | PSO           | 3         | 47.7      | 30                | 4.9 | this study|
| 0.5KrGO-PEG     | Langmuir       | PSO           | 2         | 59.5      | 30                | 4.9 | this study|

(Complimentary adsorption). The IPD model was also used in determining the rate-controlling step of the adsorption process. The model makes four assumptions: (i) there is a diffusion of adsorbate molecules from the bulk solution on to adsorbent surface, (ii) adsorbate molecules are diffused through the boundary layer to adsorbent surface, (iii) adsorbate molecules are adsorbed on active sites of the adsorbent, and (iv) adsorption is rapid initially proceeded by slow particle diffusion on to the adsorbent internal surface. In the IPD model, the rate-determining step is the slow step of adsorption and may be ascribed to intraparticle diffusion or external mechanisms such as boundary layer diffusion, complexes, and surface adsorption. A plot of q vs t0.5 revealed that the lines did not pass the origin, thus confirming that the rate-controlling step could not be solely attributed to IPD. Furthermore, all the intercept values (C) are positive, which is an indication that the boundary layer phenomenon played a crucial role in determining the adsorption rate and the adsorption occurred via a multistep adsorption process.

3.5. Adsorption Isotherm. The nonlinear fits of three 2-parameter adsorption equilibrium models (Langmuir, Freundlich, and DR) were employed to investigate the adsorbate–adsorbent interaction at equilibrium (Table 3). The Langmuir isotherm shape of the fittings could be classed as “L” based on the Giles classification system (Supporting Information 6 adsorption isotherm, Figure S6), which indicates the vertical orientation of adsorbents and strong adsorbate molecule–adsorbent site interaction.45–48 The low RSE and SSE (Table 3) showed that the Langmuir model was a well suited model. The Langmuir model assumes that (i) adsorption is monolayer, and it occurs on the surface adsorption sites of equal energy, and (ii) adsorbed molecules do not interact.49 XKrGO-PEG is highly hydrophobic with several functional groups reacting with the phenolic moiety in position C3 of olaquindox, which could also serve as the H-bond donor and acceptor to the XKrGO-PEG molecule. Another form of interaction is via the H-bond of olaquindox to XKrGO-PEG. Maximum adsorption capacity for olaquindox on 0.5KrGO-PEG obtained from the Langmuir model is 164.5 mg/g. The values of nondimensional separation factor (Ri) (Supporting Information) were used in calculating favorability factors between 0 and 1. It was observed that experimental adsorption is appropriately described by Langmuir isotherm because the Ri value obtained was between 0.016 and 0.094, an indication that adsorption was favorable.

Also, the calculated values of the dimensionless factor (Ri) for all three temperatures were between 0 and 1. These observations indicate that the experimental adsorption system is more appropriately described by Langmuir isotherm, suggesting that adsorption sites are energetically homogeneous. Table 4 shows the Langmuir adsorption capacities of this study compared to other studies with similar adsorbent materials. Based on the R² and K estimates, the values from the Freundlich model (Table 3) could reasonably describe the adsorption data. The Freundlich model assumes that adsorption occurs on a heterogeneous surface with possible multilayer adsorption. When adsorption data could be described by both the Langmuir and the Freundlich adsorption isotherms, it is assumed that the process occurred on heterogeneous adsorption sites, which have similar adsorption energies.

The DR model is used to explain whether the sorption process was a physical or chemical one.52,53 Table 3 shows the DR parameters and E values for all the adsorbents used in adsorbing olaquindox. The values obtained were below 8 kJ/mol, confirming that the adsorption was of a physical nature.

3.6. Adsorption Mechanism. An investigation of the adsorption mechanism of olaquindox on KrGO-PEG is critical, and pH studies (Figure 5) were used to provide some insight. The surface charge of the adsorbate and adsorbent can be altered by pH, which in turn affects the adsorption process electrostatically. However, in this study, insignificant changes in adsorption capacity were recorded from pH 2 to 10, implying that adsorption occurred through other means. The strong hydrophobic nature of KrGO-PEG and olaquindox promoted very strong hydrophobic interactions. Furthermore, 0.5KrGO-PEG exhibited the highest sorption capacity as compared to the other adsorbents, despite its small surface area. This is because of its highly hydrophobic nature (Table 3) due to the presence of the aromatic ring in the olaquindox structure and the significant reduction of GO-PEG. Another explanation for the high and super-fast adsorption is that hydrophobic carbonaceous materials have affinity for an adsorbate with an aromatic ring in its molecular structure,57 thus justifying the high Kf rate parameter and adsorption capacity of 0.5KrGO-PEG (Table 2).

Increased sorption capacity of olaquindox may be due to several other mechanisms, a feature not uncommon with carbonaceous/graphene-based materials. From the morphological (HRTEM) images, it was observed that reduced GO sites were altered, resulting in wrinkles, surface defects, and grove areas, which are typically characterized by high energy surface.58 These defective sites have unequal charge and energy distribution with increased chemical activity. Essentially, these defects are voids and crevices that attract high quantities of adsorbed molecules. Therefore, increased sorption capacity of 0.5KrGO-PEG can also be attributed to this structure, which promotes higher uptake of olaquindox molecules. Overall, we propose that the mechanism of interaction of olaquindox and 0.5KrGO-PEG was multifaceted and is attributed to forces such as hydrophobic and π–π interactions, defective sites on the adsorbent, and possibly pore filling; the higher the GO content, the higher the adsorption.
3.7. Adsorbent Application to Real Water Samples.
The adsorbent 0.5KrGO-PEG was tested on real water samples to determine its efficiency in the remediation of olaquindox. River water samples obtained from Umgeni River Durban, South Africa, were spiked with olaquindox, and the adsorption efficiency results were compared to GO and activated carbon used as control. River water is a complex matrix consisting of inorganic and organic materials competing for the adsorptive sites on the adsorbents; such a matrix complicates the adsorption process. On applying 0.5KrGO-PEG on river water, 68% removal efficiency was obtained. The river sample had a natural pH of ∼5, and the adsorbent application to the river water was carried out without any pH modification. The functionality of the adsorbent at any pH is very important as no further cost would be accrued through pH adjustment. The implication of non-pH adjustment in the successful remediation of olaquindox from wastewater across a broad pH spectrum is testament to the effectiveness of 0.5KrGO-PEG in real water sample remediation.

4. CONCLUSIONS
In this research, we successfully designed and characterized three-dimensional mesoporous geomedia by reducing GO-PEG in-situ and grafting it on kaolin. The geomedia have the potential to be scalable because of the cheap cost of production and the possession of multiple sites for the adsorption of organic functional groups. XKrGO-PEG exhibits improved textural properties and abundant surface functional groups, such as amide, carbonyl, and carboxyl groups, with the following advantages: (i) high efficiency for adsorption due to its hydrophobic nature; (ii) multiple removal adsorption mechanism; (iii) reusability and high stability; and (iv) application over a wide pH range. Furthermore, the adsorbent was highly efficient in the remediation of olaquindox from real and simulated water samples, with a fast equilibrium time of 30 min. Our results showed that clay-polymer geomedia are efficient, scalable, sustainable, and cheap for the remediation of organics from wastewater and in obtaining MDG 6.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c03253.

Thermogravimetric analysis, Raman spectral analysis, effect of adsorbent dose, effect of contact time, thermodynamics, engineered geomedia reusability, adsorption kinetics, and adsorption isotherm (PDF)

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Notes
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