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SYNTHESIS AND CHARACTERIZATION OF PHENOXY GROUP HERBICIDES INTERCALATED INTO CALCIUM-ALUMINIUM LAYERED DOUBLE HYDROXIDE AND ITS CONTROLLED RELEASE PROFILE

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ABSTRACT

Excessive use of commercial herbicides in agriculture can negatively impact the environment, leading to water pollution. The intercalation of herbicides, mainly 4-chlorophenoxyacetic acid (4-CPA) and 2-methyl- 4-chlorophenoxyacetic acid (MCPA) into the interlayer of calcium-aluminium layered double hydroxide (CAL) host was done to minimize the side effects by employing the controlled release profile. CAL host synthesis and the herbicide intercalation were achieved via co-precipitation method, resulting in CAL-4CPA and CAL-MCPA. The CAL host were prepared in six molar ratios (R_i) ranging from 1:1 to 1:6 using varying compositions of aluminium nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) and constant compositions of calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 6H_2O$), referred to as R_1 to R_6. The suitable ratio, R_3 was selected for the intercalation process of 4-CPA and MCPA at various concentrations of 0.025 M, 0.05 M and 0.10 M. Later, 0.025 M was selected as the optimum concentration for the intercalation of 4-CPA and MCPA at varied pH values of 11, 12 and 13. The intercalation was supported by powder X-ray diffraction (PXRD) analysis, showing an expansion of the basal spacing from 8.60 Å to 12.11 Å and 19.90 Å for CAL-4CPA and CAL-MCPA, respectively. Moreover, the absence of nitrate peak at 1326 cm^{-1} for both intercalated compounds in the Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectra has proven the intercalation. This is in agreement with the lower nitrogen content in elemental analysis and displayed high thermal stability for CAL-4CPA and CAL-MCPA. This is validated by the increase of surface area for both intercalated compounds. The surface area of CAL-4CPA obtained was 21.35 m^2g^{-1} which is larger than CAL-MCPA at 8.63 m^2g^{-1}. Furthermore, CAL-4CPA and CAL-MCPA were mesoporous material characterized as Type IV isotherm with H3 hysteresis loop and showed porous and flaky hexagonal plate-like material. Significantly, the controlled release of CAL-4CPA and CAL-MCPA were in the order of phosphate > carbonate > chloride. Both CAL-4CPA and CAL-MCPA released more rapidly in phosphate than in carbonate and chloride solution due to the influence of higher affinity and charges. The intercalated compounds of CAL-4CPA and CAL-MCPA are best fitted into the pseudo-second order kinetic model with the highest R^2 values. Overall, the findings of this study highlight the potential of CAL as a carrier host for the development of CAL-4CPA and CAL-MCPA as environmentally friendly agrochemicals that can minimize the environmental problem through modification of controlled release profile.

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CHAPTER ONE
INTRODUCTION

1.1 Research Background

The emerging field of nanomaterials and constant research in nanotechnology have demonstrated great potential in many applications. Nanotechnology is getting a significant amount of attention in material science as it can revolutionize many industry sectors such as medicine, renewable energy and information technology. Nanotechnology defines as the combination of science and engineering that involves the design, synthesis, characterization, and application of materials on a nanometer-scale or one-billionth meter (Saini et al., 2010). According to Zobir et al. (2021), nanomaterials are defined as materials having any external dimension in the nanoscale or with internal structure or surface in the nanoscale in the size range of approximately 1 nm to 100 nm. It exhibits unique properties such as chemical, physical and electronic that differ from those of bulk material which are due to its quantum size effect and surface area (Liang & Guo, 2009). It can also be classified into multiple dimensions like 0D, 1D, 2D and 3D.

On the contrary, nanocomposite is a composite material that is classified as nanomaterial. It has a multiple-phase structure with at least one phase on the nanoscale dimension (Jeevanandam et al., 2018). The nano-sized particles can be incorporated into the matrix of any standard material to promote its properties in terms of mechanical strength, thermal conductivity and physical appearance. Therefore, developed nanocomposite can possess new chemical and physical properties which are dependent on the morphology and interfacial properties. It will be greatly improved in performance, hence this shows that tailoring the materials on the nanoscale will give different properties due to their size, shape and structure. For instance, a hybrid inorganic-organic nanocomposite can be synthesized by using layered double hydroxides (LDH). LDH is a 2-dimensional unit composed of anionic clay that has shown potential in many applications, especially as host-guest compounds. The layered solids consist of positively charged layers of divalent and trivalent cations and interlayer charge-compensating anions (Li et al., 2004).

In this research, calcium-aluminium-LDH (CAL) served as an inorganic host