Applied Clay Science xxx (2013) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Review article

Adsorption of proteins and nucleic acids on clay minerals and their interactions: A review

Wei Hua Yu [a,b], Na Li [b], Dong Shen Tong [b], Chun Hui Zhou [b,*], Chun Xiang (Cynthia) Lin [c], Chuan Yun Xu [d]

[a] Zhijiang College, Zhejiang University of Technology, Hangzhou 310024, PR China
[b] Research Group for Advanced Materials & Sustainable Catalysis (AMSC), College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Hangzhou 310014, PR China
[c] School of Chemical Engineering, The University of Queensland, St Lucia, Brisbane, Queensland 4067, Australia
[d] Key Laboratory of Clay Minerals of Ministry of Land and Resources of The People's Republic of China, Zhejiang Institute of Geology and Mineral Resources, Hangzhou, 310007, Zhejiang, China

ARTICLE INFO

Article history:
Received 14 January 2013
Received in revised form 23 April 2013
Accepted 1 June 2013
Available online xxxx

Keywords:
Clay mineral
Biomolecule
Adsorption
Protein
Nucleic acids
Mechanism

ABSTRACT

The understanding of adsorption of proteins and nucleic acids on clay minerals and their interactions is important in biological applications for soil ecosystem, the earth's biochemical evolution and origin of life, delivery of drug, etc. This review summarizes adsorption of proteins and nucleic acids (DNA, RNA) on natural clay minerals of layer phyllosilicates such as montmorillonite, kaolinite and illite and their interactions. Recent advances in adsorption mechanisms, adsorption sites and effect of various factors on adsorption are discussed. The interaction mechanisms are suggested to be cation exchange, electrostatic interactions, hydrophobic/hydrophilic interactions, ligand exchange, cation bridge, water bridge, hydrogen bond and van der Waals forces. The physical and chemical characteristics of clay minerals and proteins and nucleic acids are mainly responsible for the absorption of these biomolecules by clay minerals besides external conditions, for instance pH and ion strength of absorption solution. Finally, comments on the perspectives and potential benefits of the studies on adsorption of proteins and nucleic acids on clay minerals and their interactions are also made.

1. Introduction

Naturally abundant clay minerals such as montmorillonite, kaolinite and illite are a class of layered alumosilicates possessing good biocompatibility, strong adsorption, ion exchange ability and expansibility (Ertem, 2004; Tran et al., 2012; Zhang et al., 2010; Zhou, 2011; Zhou and Keeling, 2013; Zhou et al., 2012). They can adsorb various biomolecules including proteins, DNAs and RNAs in natural environment (Biondi et al., 2007; Cai et al., 2008; Wu et al., 2012). The studies on adsorption of these biomolecules by clay minerals play an active role in the soil ecosystem safety, the earth's biochemical evolution and origin of life, the drug delivery systems, enzyme immobilization, protein fractionation and even gene-engineering.

1.1. Soil ecosystem safety

Nucleic acid molecules (DNAs and RNAs) and proteins are bioproduced and bioactive macromolecules. In soil, their presence can be due to the liberation by excretion from microorganisms, plants, and animals or by lysis of dying cells (Recorbet et al., 1993; Widmer et al., 1996). The adsorption of extracellular DNA and RNA molecules and proteins on the surface active particles of clay minerals have received much attention (Mignon and Sodupe, 2012; Paget et al., 1998). Nucleic acid molecules and proteins adsorbed by clay minerals can persist for a long time in hostile environments and maintain their biological activities such as the ability to transform competent bacterial cells, to transmit the genetic information contained in their sequences and to interact with molecules in the soil environment (Cai et al., 2006a; Franchi and Gallori, 2004; Pietramellara et al., 2007; Vettori et al., 1996). With the increasing commercial applications of transgenic plants, it is necessary for soil ecosystem security to study the adsorption and desorption mechanisms of nucleic acid molecules and recombinant proteins released from transgenic plants on clay surface in soils. The binding of these biomolecules by clay minerals will influence cultures of soil microorganisms and reduce their availability as a source of carbon and/or nitrogen for microbe (Fiorito et al., 2008; Scappini et al., 2004; Stotzky, 2004).

1.2. Earth's biochemical evolution and origin of life

Clay minerals such as montmorillonite on the prebiotic earth might play a central role in the formation of proteins and nucleic acids (Hashizume et al., 2010; Lahav et al., 1978; Moore and Steitz, 2002; Sciascia et al., 2011). They might have served as primitive vessels for

* Corresponding author.
E-mail address: clayton.zhou@yahoo.com.au (C.H. Zhou).

0169-1317/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.clay.2013.06.003

amino acids, purines, and pyrimidines. They concentrated these biomolecules on their surface and catalyzed the polymerization of biomolecules. Biomolecule–clay mineral complexes provide protection against strong radiation, bio- or photodegradation and inactivation (Ferris et al., 1996; Hanczyc et al., 2003; Huang and Ferris, 2003; Saladino et al., 2004). In other words, clay minerals help synthesis and preservation of biopolymers which finally lead to the origin of life on the earth (Ferris, 2002; Franchi and Gallori, 2005).

1.3. Drug delivery systems

Gene drugs represent a new potential therapeutic strategy for cancer, genetic diseases, neurodegenerative disorders or infectious diseases. Over the recent years, clay minerals used as potential nano-sized carriers for genes have captured increasing attention. Binding and adsorption of DNAs onto clay minerals as structurally stable gene delivery systems can avoid decomposing in the highly acidic environment of stomach or nuclease/enzyme degradation before drugs reach the intended destinations. They can also secure the release of high local concentrations of gene drugs at the targets for therapeutic purposes (Aguzzi et al., 2007; Slowing et al., 2008; Xu et al., 2008). For example, for the complex of montmorillonite and plasmid DNA encoding the enhanced green fluorescent protein (EGFP) gene, montmorillonite acted as a novel vector for an oral gene-delivery system. In this system, the EGFP gene was expressed in the small intestine, indicating that montmorillonite protected the plasmid DNA from the acidic environment in the stomach and DNA-degrading enzymes in the intestine. As a result, the plasmid DNA was successfully delivered into cells of the small intestine (Kawase et al., 2004). In addition, inorganic clays used as non-viral vectors for in vivo gene therapy have advantages in their safety, simplicity and big DNA packaging capacity (Masago et al., 2007). Clay minerals have been successfully used as non-viral vectors for the delivery of gene drugs to cells in recent studies to solve problems of adverse side effects such as severe immunological and toxicological responses even the death of a patient which happened on viral vector (Saul et al., 2007; Swadling et al., 2010). For example, a non-viral gene transfer system was developed by the adsorption of DNA molecules into the hexadecyltrimethylammonium (HDTMA)–montmorillonite (MMT) complexes and the DNA molecules were successfully transfected into the nucleus of human dermal fibroblast without degradation by nuclease (Lin et al., 2006). Liu et al. (2011) claimed that the oligo(styrene-co-acrylonitrile)-modified montmorillonite could be a promising candidate of biosafety controlled-release carrier for gene delivery by evaluating the cytotoxic effect of the modified montmorillonite on transcriptional activity of apoptosis-related gene and apoptosis-related protein and mRNA level. Besides, binding of proteins including pharmaceutical peptides and growth factors onto clay minerals used as drug release system has been reported. Adsorption of the protein of epidermal growth factor onto montmorillonite clay platelets played a critical role in tissue regeneration (Vaiana et al., 2011).

1.4. Other applications

Adsorption and binding of nucleic acids and protein molecules by clay minerals have many other applications. They can be used in enzyme immobilization (Sinegani et al., 2005), protein fractionation (Barral et al., 2008; Causserand et al., 2001), adsorption of protein in wine and poultry industry (Rytwo et al., 2010; Tran et al., 2012), high density genetic information storage (Choy et al., 2007), biosensing (Mousty, 2010) and other bionanocomposites and biofunctional materials (Kolman et al., 2012).

Studies on the adsorption and binding of the biomolecules by clay minerals have many applications and can help in the understanding of the origin of life. This review is focused on recent findings on the interactions between clay minerals of montmorillonite, kaolinite and illite and biomolecules including proteins and nucleic acids. Advancement in this field provides deep insights into the effects of various factors on adsorption of biomolecules by clay minerals.

2. Interactions between clay minerals and proteins

2.1. Binding forces

Adsorption and binding of protein molecules by clay minerals are involved in a variety of physical and chemical interactions such as cation exchange, electrostatic interactions, hydrophobic affinity, hydrogen bonding and van der Waals forces, etc. Table 1 lists possible adsorption mechanisms of protein molecules by clay minerals.

In general, small protein molecules with positive charge can be intercalated into the interlayer of montmorillonite through cation exchange. It should also be noted that the amount of adsorbed proteins can commonly exceed the cation exchange (CEC) of montmorillonite (Johnston et al., 2012). Therefore, cation exchange cannot be the only factor in adsorption of proteins onto montmorillonite.

Because clay minerals have permanent negative and variable surface charge, charged protein molecules can be adsorbed by clay minerals via electrostatic interactions. It depends on the negatively and positively charged states of protein molecules in environment with adsorption pH (Benetoli et al., 2007; Wang and Lee, 1993).

In addition to cation exchange and electrostatic forces, the presence of 'hydrophobic region' and 'hydrophilic region' on the clay mineral surface is also responsible for adsorption of protein molecules by clay minerals (De Oliveira et al., 2005; Quiquampoix et al., 1993). Clay minerals are capable of binding polar protein molecules since the octahedral surface is hydrophilic while the tetrahedral surface with hydroxyl groups is hydrophobic. The exchangeable cations in the interlayer space balancing the charge deficit of the layers of clay minerals have a hydrophilic character (Servagent-Noinville et al., 2000), while the uncharged regions between charge sites present a partial hydrophobic character (Bajpai and Sachdeva, 2002a; Van Oss and Giese, 1995). Protein is composed of amino acids with different polarity. Intramolecularly non-polar amino acid side chains of the protein form hydrophobic region, whereas polar amino acids provide hydrophilic surface. The hydrophobic action between non-polar and polar amino acids plays a leading role in controlling the structural stability of protein in solution. The hydrophilic portion of the clay surface interacts with the positively charged side chains of the protein (Bleam, 1990). On the other hand, the hydrophobic character of clay surface could be removed by the positively charged side chains of the protein molecules (Dumat et al., 2000). The adherence of protein molecules spontaneously to the hydrophobic regions of clay minerals can reduce free energy of the system through a spontaneous thermodynamic process in order to remain structural stability. Therefore, the hydrophobic interaction between the protein and the siloxane surface of clay mineral mainly governs adsorption, which can compensate the electrostatic repulsion of negative charge between protein and clay mineral surface (Adélia et al., 2003; Botella et al., 2004). In addition, hydrogen bonding and van der Waal forces have been proved to be important in binding of proteins onto clay minerals. van der Waals forces afford a partial overlap of the electrostatic repulsion.

2.2. Binding sites

In many cases, there are two main adsorption sites: the interlamellar channels and external surfaces including broken edge and planar surface of clay minerals (see Fig. 1). Which sites on clay minerals play a dominant role in the adsorption depend on structure and property of both clay minerals and protein molecules.

Different clay minerals have different adsorption sites. The adsorption sites on kaolinite and illite are only external surface due to their non-expanding layers. Smectites such as montmorillonite and

Please cite this article as: Yu, W.H., et al., Adsorption of proteins and nucleic acids on clay minerals and their interactions: A review, Applied Clay Science (2013), http://dx.doi.org/10.1016/j.clay.2013.06.003